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THE

PHYSICAL REVIEW.

THE EFFECT OF THE INTENSITY UPON THE VELOCITY OF LIGHT.

By Thomas E. Doubt.

ANY measurement giving information upon that very important physical magnitude, the velocity of light, will aid the progress of physics. The relation between the intensity of light and its velocity of propagation is one of fundamental importance.

The most searching examination that has been made thus far into the effect of the intensity upon the velocity of light was that by Ebert.[1]

He tested for the effect of the intensity upon the velocity of light to one part in 860,000, where the intensity was varied in the ratio of one to twenty. Thallium light was employed as a source. In another experiment with light from a mercury spark (Hg α) the effect was tested for to one part in 840,000, where the intensity was varied in the ratio of one to two hundred fifty. He used many other sources of monochromatic light but in no case was the test carried to anything like the same degree of accuracy. His conclusion was "That the wave-length and therefore the velocity of propagation of light is to nearly a millionth part independent of its intensity when this is varied in the ratio of one to two hundred fifty."

The work of Ebert greatly exceeds in accuracy that of Lippich[2] or that of Muller.[3]

[1] Wied. Ann., 1887, No. 32, p. 336.
[2] Wien. Ber., 1875, 272, p. 355.
[3] Pogg. Ann., 1872, p. 145.

Professor Michelson suggested that the effect of the intensity upon the velocity of light could be tested for with a much higher degree of accuracy by the aid of a form of interferometer such as was used in measuring the effect of the motion of the medium upon the velocity of light.[1]

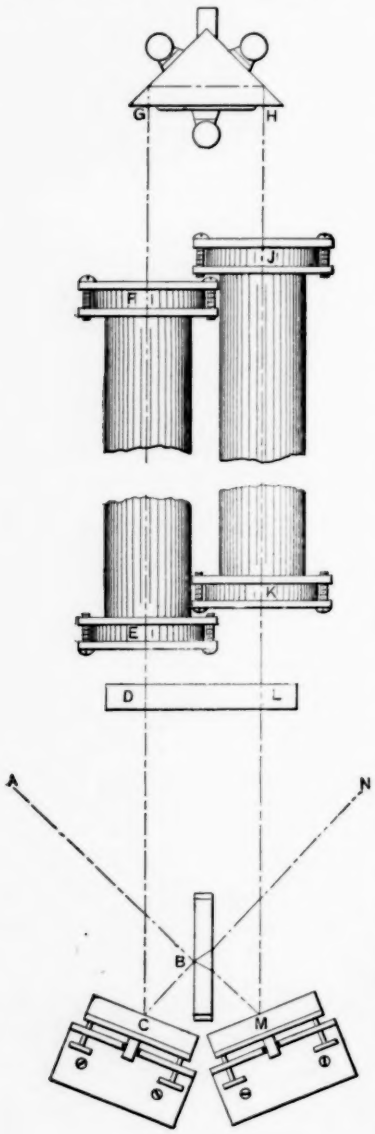


Fig. 1.

DESCRIPTION OF APPARATUS.

The form of apparatus used in this research is very similar to that used by Michelson and Morley in their investigation of the motion of the medium upon the velocity of light. Light from a source in the direction *A* (Fig. 1) meets the half-silvered surface *B* where it is separated into two portions. One part travels by the path *CDEFGHJKLMB* and the other by the path *MLKJHGFEDCB*. At the dividing glass *B* the two portions are reunited and are observed from the direction *N* by the eye or telescope. The reflecting surfaces *C* and *M* are plane glass silvered upon their front faces. *GH* is a large rectangular prism. *EF* and *KL* are brass tubes about 4.5 cm. in diameter with their ends closed with plane parallel glass plates. *DL* is a large plane parallel plate of glass silvered upon one surface in strips. One strip above is silvered so as to allow only one beam to pass through unhindered and similarly a strip below is silvered so as to allow the other beam free passage.

[1] Am. Jour. Sc. (3), Vol. XXXI., 1886.

This silvered surface is used for reducing the intensity of one beam before it passes through the apparatus while the beam passing in the opposite direction is not reduced until it passes over the very large optical path. Numerous smaller plane parallel plates of glass silvered in strips were also introduced, usually only in one path at a time. Since the paths are identical it can make no difference with the center of the central fringe whether the plates are introduced at D or at L. In general, the introduction of a glass plate into the path of either beam will produce a change in the width of the fringes or a rotation of the fringes about some central point or both change and rotation.

The advantages of this arrangement are very marked. The apparatus permits the use of an extended source of light such as a gas flame, an arc light or sun light. Again it allows of a very large path over which the beams pass in different conditions and are then brought to the separating glass where they are made to interfere. One beam travels over a very large path with small intensity while the other travels over the same path with great intensity.

Adjustments and Observations.

The source of light was adjusted so as to give a beam meeting the dividing surface at an angle of 45°. All the surfaces were made approximately vertical. The rectangular prism was placed at a sufficient distance from the dividing surface upon a leveling table. The mirrors and prisms were respectively supported by brick piers. The mirrors at C and M were adjusted so as to give sharp vertical fringes. The plate DL was then placed in the path of the beam and both beams were allowed to pass through the clear portion and the plate was adjusted until the fringes were again vertical and sharp. The position of the central fringe was noted and the plate moved carefully so as to cause a silver strip to intercept one path. The position of the central fringe was noted.

This procedure was carried out first with air between the rectangular prism and the mirrors, the distance between them being about 220 cm. For very dense silver films the selective absorption was noticeable but with films of medium density the effect was much the same as if a light cloud had come over the sun, the

intensity only being cut down and the colors changed but little. This effect of selective absorption is more noticeable when determining the amount of transmitted light by means of the photometer. The total optical path over which the two beams pass in different conditions is 460 cm. This was calculated by taking into account the distance in glass and its refractive index as well as the distance in air. If the mean wave-length is taken as .000057 cm. the optical path is over eight million wave-lengths. If it is assumed that a shifting of one thirtieth of the width of a fringe may be readily detected then a change in velocity of one in 240 million could be detected or a change of 240 cm. per sec.

In estimating the sensitiveness of the method a series of settings of the eye-piece micrometer of the observing telescope was made on the dark fringes bordering on the central fringe. The intersection of the diagonal cross wires (Fig. 2) was used to determine the location of the fringes. This figure represents the field of view of the telescope with two vertical wires attached to the micrometer removed so as to represent the fringes more clearly. The fringes were usually so adjusted that there were seven in the field of view.

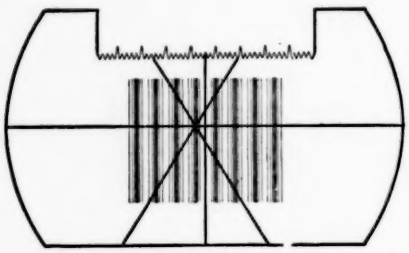


Fig. 2.

The following results were obtained with white light:

Reading of micrometer head with three turns between each setting increasing from left to right.

		Width of Central Fringe.	Difference from Mean.
Left.	74.4	377.2	−19.1
Right.	52.6	392.6	− 3.7
Left.	60.0	394.6	− 1.7
Right.	54.6	399.0	2.7
Left.	64.4	408.6	12.3
Right.	63.2	402.5	6.2
Left.	60.3	400.7	3.4
Right.	61.4		
		Mean 396.3	Variation 7.01

The sum of the differences is 589.52. The mean error of one observation is 9.81 or 2.5 per cent. The probable error of the result is 1.18 or .29 per cent. One would seem justified in concluding from the above results that if a shifting of a hundredth of the width of a fringe took place it could be detected. In what follows I have assumed that a shifting of one thirtieth of a fringe could be detected with certainty.

A large number of silver films were used of increasing opacity until one was found through which the light could barely produce visible interference fringes. The amount of light transmitted by the silver film was measured by Glan's Photometer. The film allowed one part in 290,000 to pass through. Thus one beam travels over a path of 460 cm. with an intensity only one part in 290,000 of that of the other beam and if a change in velocity of 124 cm. per sec. occurred it could be detected. No shifting of the central fringe was observed.

The tubes were now introduced and the experiment repeated. The tubes contained air. No new facts develop. The fringes were somewhat steadier with the tubes in the path than without them. When the tubes are filled with distilled water the optical path is greater than with air. The tubes in one case were each 200 cm. in length. The optical path amounted to 593.4 cm. or 10,400,000 wave-lengths in air. If a change in intensity produced a change in velocity of 100 cm. per sec. it could be detected.

The results of the two sets of experiments may be tabulated in the following manner:

Ratio of Intensities.		Length of Optical Path.	Change of Velocity that Might be Detected.
Air	1:290000	460 cm.	124 cm. per sec.
Air	1:290000	1000 "	57 " " "
Water	1:250000	593 "	100 " " "
Water	1:43000	1289 "	42 " " "
Carbon disulphide	1:43000	707 "	80 " " "

The experiment was tried by adjusting the fringes so that they made an angle with the vertical. The silver film was inserted and the position of the central fringe was noted. No displacement was noted at angles of about 45° or 135° or when the fringes were

horizontal. Hence it may be concluded that change of azimuth has no effect.

These experimental results for light traveling in air justify the conclusion that a change in intensity of one in 290,000 does not change its velocity by 57 cm. per sec. In the case of water a change in intensity of one in 43,000 does not produce a change of 42 cm. per sec. In the case of carbon disulphide the same change in intensity does not produce a change in velocity of 80 cm. per sec. It seems very probable from the settings taken with the eye-piece micrometer that a shifting of one fiftieth of the width of a fringe could be detected. Hence a change in intensity from 1 to 40,000 in water does not affect the velocity to one part in 1000 million.

Grateful acknowledgments are due Professor Michelson for his helpful suggestions. Much assistance has been received from Dr. Mann and the staff of Ryerson Physical Laboratory.

UNIVERSITY OF CHICAGO,
May 4, 1903.

ON THE NATURE OF CERTAIN RADIATIONS FROM THE SULPHATE OF QUININE.

By Fanny Cook Gates.

IN studying the properties of certain substances known to become phosphorescent by a change in temperature, G. Le Bon found that when the sulphate of quinine is either heated or cooled through a high range of temperature, it becomes temporarily phosphorescent and possesses the power of discharging the leaves of an electroscope. He believed this effect to be due to chemical reaction, dehydration taking place when the quinine is heated above 100° C. and hydration upon cooling it again, and from this he argued that the radiations from radium and the other active minerals may be due to slight internal temperature changes and entirely explained by chemical reactions.

The ionization of the gas is the accompaniment of so many phenomena of totally different origin and character that before such a theory as M. Le Bon advances can be tenable to any degree, it must be proved that the radiations he describes possess other properties characteristic of those from the naturally radio-active substances, in addition to the property of causing the surrounding air to become a conductor of electricity. The experiments described in the following pages were undertaken for the purpose of determining the exact nature of the radiations emitted by the quinine sulphate under the conditions named, and of ascertaining to what extent they are similar to those given off from the radio-active substances.

The first tests were made with one gram of quinine sifted uniformly over a metal plate 20 cm. square. This was heated over a spirit lamp and then allowed to cool to the temperature of the room between parallel metal plates within a closed vessel. The plates were about 5 cm. apart and insulated. The lower one on which the quinine rested was joined to one terminal of a storage battery of 300 volts and the upper one to the electrometer, other

connections being made in the usual manner. The strength of the current passing between the plates as indicated by the deflection of the electrometer was used as a measure of the rate of radiation from the quinine.

With the apparatus arranged as above described, it was found that after removing the quinine from the source of heat no deflection of the electrometer was at first produced, but that after about two minutes a slight current was noticed which increased slowly at first and then rose suddenly to a maximum at the end of about five minutes. It then rapidly decreased and the effect apparently ceased altogether after fifteen minutes. This variation of the radiation

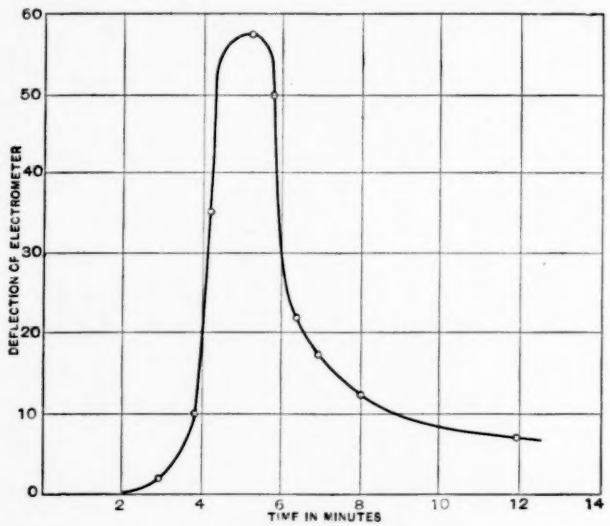


Fig. 1.

with time is shown in Fig. 1. On account of the rapid rate of change in current while passing through its maximum value, it was impossible to make accurate determinations near that point and the curve gives its value only approximately.

Upon reheating the same quinine and observing under apparently similar conditions, it was found that although curves of the same general type were obtained, the total radiation produced during successive tests varied greatly. This seemed to indicate either that repeated heatings of the quinine changed its power to emit rays or that slight differences in the temperature to which it was heated

produced comparatively large changes in the resulting radiation. For this reason the spirit lamp was discarded and the quinine was heated to a definite temperature in a hot air bath. When allowed to cool from this temperature successive tests of the same substance gave curves of the same magnitude showing that the treatment had caused no inherent change in the quinine and that a slight variation in the temperature range produced a definite change in the resulting radiation.

Range and Rate of Cooling.

By the range of cooling, is meant the total number of degrees through which the quinine is cooled during a single test. The rate of cooling is the fall in temperature per second.

As has been stated, the ionization of the surrounding air is produced during the process of heating as well as that of cooling the quinine, but the experimental difficulties in obtaining accurate measurements of the radiation were so much greater in the former process than in the latter, that we have here confined our attention to the results obtained during cooling.

Two series of tests were made in which the temperature range was made to vary. In the first set the upper temperature was changed for each test while the lower one was kept always the same. In the second set the upper temperature was kept constant, and the effect noted by cooling the quinine from this temperature to different lower ones. This was accomplished by placing the parallel plates, between which the ionization took place, inside an air-bath the temperature of which could be regulated. These observations made it possible not only to test the effect of increasing the range and the rate of cooling, but to compare the effects produced by equal falls in different parts of the scale, and thus to determine where the maximum radiation is produced.

From the first set of observations, about 180° C. was found to be the highest temperature to which the quinine could be heated without permanent chemical change, and no appreciable radiation was observed unless the quinine was heated above 70° C. A comparison of the currents observed at the end of four different temperature ranges, each having the same lower limit is given in the

following table. The current is here measured in an arbitrary unit of the order of 10^{-13} amperes and in each case the current at the end of five minutes after heating is approximately the maximum current for that test.

Upper Temperature.	Lower Temperature.	Range.	Current After 5 Minutes.	Current After 10 Minutes.
180° C.	18° C.	162°	75	20
165	18	147	50	16
100	18	82	20	11
75	18	57	10	7.5

From the second series of experiments due to changing the lower temperature of each cooling, a normal fall from 180° C. to 50° C. was found to produce but little effect, but when the lower limit was

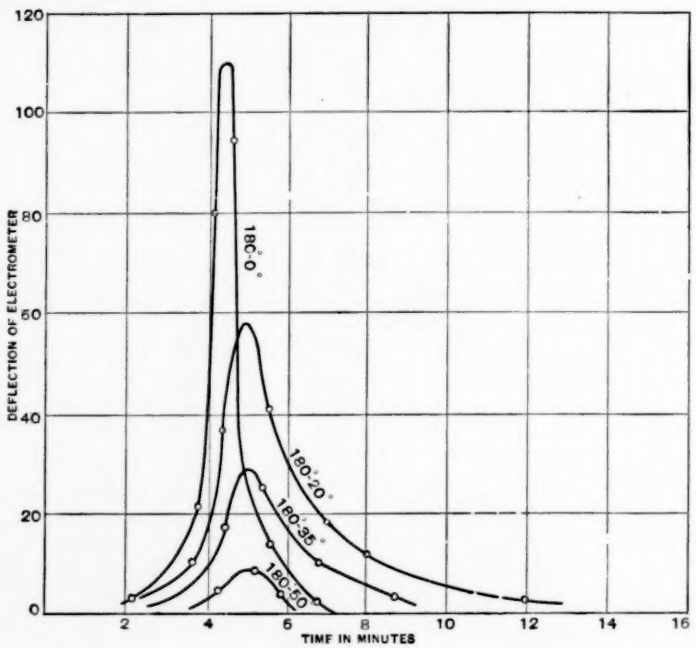


Fig. 2.

below 40° an increase in the range produced a rapid increase in the current. The total quantity of electricity discharged by the rays however did not increase when the lower temperature was below 18° or 20°. Thereafter an increased rate of radiation due to an increased rate of cooling was counterbalanced by a decrease in the

time during which the radiation continued. The curves shown in Fig. 2 illustrate this. When cooled to 0°, the maximum current was nearly twice as great as when cooled to 20°, but the effect lasted only half as long. A similar but more marked effect was observed when the testing plates were placed over a vessel containing liquid air. In this case the current rose almost immediately to a high maximum value, but the effect apparently ceased within three minutes. Thus it would seem that *the total radiation is not increased by an increase in range when the lower limit is below 20°.*

The fact that an increase in the range from 180° to a point below

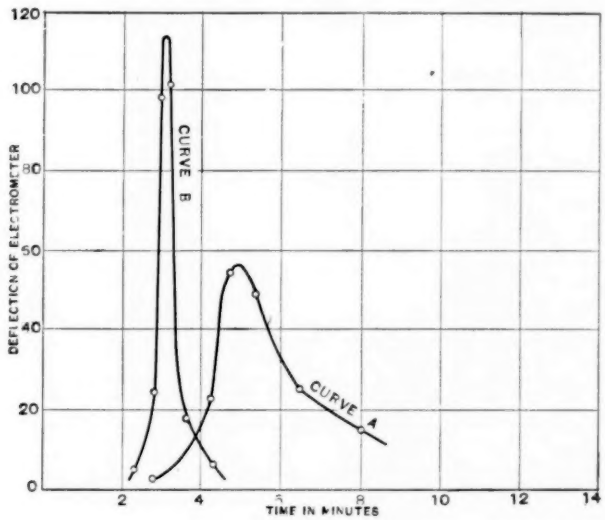


Fig. 3.

20° increased the rate of radiation at the expense of the time it continued would be entirely explained by the increased rate of cooling, providing the rate of radiation is solely determined by the rate of cooling during a given change. Direct experiments were therefore made in which the cooling was hastened by blowing dry dust-free air between the parallel electrodes as soon as the quinine was in place. In Fig. 3, Curve A shows the rate of radiation under normal cooling, while B is the curve when the cooling was hastened in the manner described, the range being the same. The similarity of the latter curve with that in Fig. 2 caused by the 180°–0°

range is striking and strongly indicates that *an increase in the rate of cooling increases the rate of radiation but does not change the total radiation during a single cooling.*

Consistent with these results were those obtained by using very thin layers of quinine. One fifth of a gram scattered over a given area was found to give as large a maximum current as that derived from one gram over the same space, but the radiation continued for a correspondingly shorter time. This is entirely explained by the more rapid cooling of the thin than of the thick layer. When heated on a thick metal plate the effect was less than when a thin plate was used, presumably because it retained the heat and retarded the cooling. Plates of different metals of uniform thickness gave no appreciable difference in the radiation. Similar but more marked results were obtained by saturating the air of the testing vessel with water-vapor, and also by spraying the quinine itself with water. In both cases the decay of the radiation was hastened.

The above results were all obtained with an air space between electrodes of about two inches and a potential difference of 300 volts. By attaching the upper plate to an insulated screw of known pitch it was possible to vary the distance between the plates as much as desired. Before this question of the absorption in air could be satisfactorily investigated it was necessary to determine the effect produced by increasing the P.D. between the electrodes.

EFFECT OF VOLTAGE. SATURATION CURVE.

One of the chief characteristics of the radiations from the active

Voltage.	Current After 10 Minutes.				
	First Test.	Second.	Third.	Average.	Ratio.
900	32.0	33.5	32.8	32.8	100
600	23.5	23.9	24.0	23.8	72
300	13.0	13.7	13.4	13.4	41
Voltage.	**Current After 5 Minutes.**				
900	21.5	21.5	23.5	22.2	100
600	15.5	15.7	17.0	16.1	72
300	8.5	9.2	9.5	9.1	41

elements is that after a certain strength of electric field is attained a further increase in the potential difference will not increase the

ionization current; that is, a saturation current is obtained which cannot be increased with voltage.

The effect of voltage on the radiations from quinine sulphate was found to be very different, as will be seen from the tabulated results obtained from three coolings of the same quinine, during which the potential difference was each time varied. These results on a current voltage diagram (Fig. 4) give no indication of a saturation value to the current, although the strength of the field is about

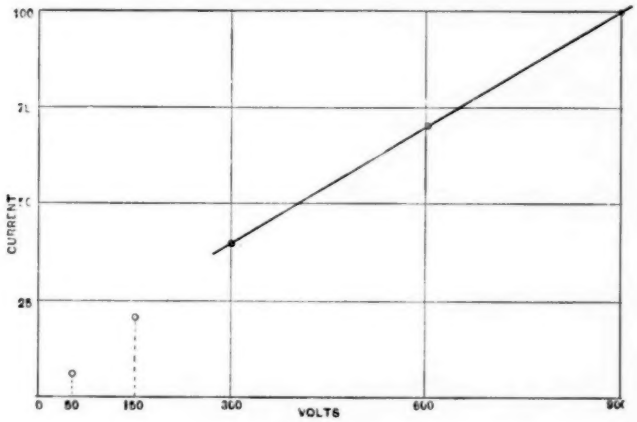


Fig. 4.

twenty times as great as that sufficient to produce saturation for radium radiations under similar conditions.

Observations were made with various widths of air space, but although the plates were brought to within 2 mm. of each other, no indication of saturation was obtained for a P.D. as great as 900 volts. An attempt was also made to determine whether with low voltages, the current might not vary as the square of the P.D. but no definite results could be obtained. With 150 and 50 volts respectively the values found for the current when expressed in ratio as above were 21 and 5 (see Fig. 4).

Absorption by Air and other Substances.

Since no saturation current could be obtained it was impossible to secure a value of the coefficient of absorption in air, but by varying the width of the air space and keeping a constant potential difference between the plates, results were obtained which were a

marked contrast to those produced with the uranium, thorium and radium radiations.

As has already been stated all observable effect from the quinine ceased within fifteen minutes of the time of heating when the distance between the plates was 5 cm. When the width of the air space was reduced to one half of this value the value of the maximum current was approximately doubled, and the electrometer deflection was easily observed for thirty or forty minutes. When the electrodes were only 3 mm. apart the effect was clearly observed for over two hours. The actual numerical values obtained from observations with a P.D. of 900 volts are shown in the following table:

Distance in Centimeters Between Electrodes.	Current After 10 Minutes.	Current After 20 Minutes.
5.0	1.6	1.0
2.5	7.4	4.5
1.2	14.0	10.5
.3	32.0	20.0

With the electrodes 3 mm. apart and with a potential difference of 900 volts between them, a sheet of aluminum foil only .003 mm. thick was found to cut out all effect and the radiations were also found to be unable to penetrate a thin sheet of paper. This offers perhaps the most striking contrast between the two types of radiations since the most easily absorbed rays from radio-active substances will penetrate several layers of aluminum foil with comparatively little loss in intensity.

Both quartz and glass plates 2 mm. thick were placed over the quinine in turn and although no deflection of the electrometer was produced these results can carry no evidence one way or the other since the conditions prevented a sufficiently rapid rate of cooling.

DIRECTION OF THE ELECTRIC FIELD.

One of the most unexpected and suggestive phenomena connected with the radiations under discussion is that caused by changing the direction of the electric field. When the plate on which the quinine rested was joined to the positive pole of the battery, the resulting ionization was invariably greater than when joined to the negative pole. This effect was more marked when

the plates were far apart, but even when the space between the electrodes was only 3 mm., the ratio of the current obtained by joining the lower plate to the positive pole of a 600-volt battery to that obtained by joining it to the negative pole was 1.2. This ratio for other distances is shown in the following table:

Distances in Centimeters Between Electrodes.	Ratio.
.3	1.20
1.2	1.48
2.5	1.64
3.7	1.93
7.5	2.53

This marked effect indicates that the radiations may possibly be produced by ultra-violet light. The current voltage curves are very similar to those obtained when ultra-violet light falls on a charged surface, except that here both positive and negative ions are present. The difficulty in obtaining saturation may be due to the fact that the ionization takes place very close to the surface of the quinine and the ions consequently rapidly diffuse to its surface and cannot be removed without a very intense field. The difference in the positive and negative currents is probably due to a difference in the size of the positive and negative ions, the positive ions traveling faster than the negative ones. A difference in their size could be explained by the condensation of vapor around them in the same way as the ions in flame gases increase in size when the gases cool. The whole effect appears to be due to some type of radiation which is easily absorbed in the gas and since the electrical effects are accompanied by marked phosphorescence it seems possible to suppose that the ionization may be caused by very short waves of ultra-violet light such as Lenard has shown to be active in ionizing the gas.

Optical Effect.

Mention has been made of the phosphorescence accompanying this phenomenon. The quinine when heated in a dark room was observed to glow for about fifteen minutes while cooling. The light given off was bluish white in color but was of insufficient intensity to admit of optical measurement.

Summary.

In conclusion let us contrast those properties found to be most characteristic of the quinine radiations with those obtained under similiar conditions from radio-active bodies.

1. The quinine radiations are only apparent when accompanied by a great temperature change. The rate of ionization varies during this change and in a short time the effect ceases altogether. The rate of discharge of electricity between plates exposed to the radiations from the active elements, however, is incapable of alteration by any change in temperature, and so far as is known these radiations suffer no alteration with time.

2. By increasing the strength of the electric field it is impossible to secure a maximum ionization current from quinine radiations while a comparatively weak electric field is sufficient to produce a saturation current due to the radiations from radium and the other active elements.

3. The quinine radiations are certainly largely absorbed by at least two or three mm. of air and may be absorbed by a much shorter distance, while the least penetrating radiations from the active elements will pass through several cm. of air without great loss in intensity.

4. The quinine radiations are completely absorbed by a very thin sheet of aluminum which does not cut out the rays of uranium, radium and thorium.

5. The rate of ionization due to radium radiations is independent of the direction of the field, whereas that from quinine radiations undergoes a marked change upon reversing the direction of the field.

These conclusions show very clearly that there is no evidence for believing that the ionization from quinine radiations is due to the spontaneous projection of charged masses from the atom as in the case of radio-active bodies, but to molecular actions which are influenced by temperature.

While M. Le Bon is therefore undoubtedly correct in his assertion as to the nature of the cause of the quinine radiations, these experiments show no justification whatever for attributing the radiations from radium and the other active bodies to a similar cause, but on the contrary testify to a fundamental difference in production.

I desire to express my deep obligation to Professor Rutherford for his kind interest and direction during the course of these experiments.

MacDonald Physics Building,
McGill University, June, 1903.

A STUDY OF THE MOLECULAR LOWERING OF THE FREEZING-POINT OF WATER PRODUCED BY CONCENTRATED SOLUTIONS OF ELECTROLYTES.

By Harry C. Jones and Frederick H. Getman.

Historical Review.

In applying the freezing-point method to the then newly discovered theory of electrolytic dissociation Arrhenius[1] noted that the molecular depressions for solutions of calcium, strontium and magnesium chlorides, and cadmium iodide decrease with increasing concentration to a certain minimum value and then increase again.

Arrhenius[2] found that solutions of cane-sugar, dextrose, mannite and glycerine also exhibit this same phenomenon. Raoult[3] observed this abnormality in his studies on the freezing-point depressions of calcium nitrate, magnesium sulphate and copper sulphate.

Other workers in this field have made the same observations. Among these may be mentioned Loomis,[4] Barnes,[5] Jones,[6] Jones and Ota,[7] Jones and Knight[8] and Ponsot.[9]

The first systematic study of this phenomenon, however, was made by Jones and Chambers[10] in 1900.

They determined the molecular depressions for solutions of calcium, barium, strontium, magnesium and cadmium chlorides and bromides, the concentrations varying from $\frac{1}{500}$ normal to normal.

[1] Ztschr. phys. Chem., 2, 496.
[2] Ibid., 2, 495.
[3] Ibid., 2, 488.
[4] Wied. Ann., 57, 503.
[5] Trans. Roy. Soc. of Canada, Vol. VI., Sec. III., 37.
[6] Ztschr. phys. Chem., 12, 642.
[7] Amer. Chem. Jour., 22, 5, 1899.
[8] Ibid., 22, 110, 1899.
[9] Recherches sur les congélations, Paris, 1896.
[10] Amer. Chem. Journ., 23, 89, 1900.

With all the salts, except cadmium chloride and bromide, minima were found. In addition to determining the molecular depressions for these solutions the authors also measured the conductivities in order to see whether there existed any irregularity in the conductivity curves in the same region of concentration where the abnormal depressions became manifest. To quote their own words: "An examination of the conductivity curves shows no irregularity in the region where the molecular lowering of the freezing-point becomes a minimum. The conductivity curves are just such as would be expected for any strongly dissociated electrolyte in water. The conductivity increases regularly from the most concentrated to the most dilute solution investigated, and shows a continually increasing dissociation with increase in dilution."

The work of Jones and Chambers was extended by Chambers and Frazer,[1] who studied hydrochloric and phosphoric acids, sodium acetate, copper sulphate, zinc chloride, strontium and cadmium iodides. In each one of these cases a more or less well defined minimum was observed. In 1902 W. Biltz[2] published the results of his further extension of the work inaugurated by Jones and Chambers. He, together with Julius Meyer, studied the following substances: Cassium chloride, rubidium chloride, potassium chloride, ammonium chloride, sodium chloride, lithium chloride, mercuric chloride, cupric chloride, zinc chloride, manganous chloride, nickel chloride, cobalt chloride, ferrous chloride, aluminium bromide, cupric bromide, potassium sulphocyanate, potassium cyanide, potassium bromide, potassium iodide, potassium fluoride, lithium nitrate, lithium bromide and lithium iodide.

The concentrations varied from $\frac{5}{100}$ normal to $\frac{3}{2}$ normal. In almost every case well marked minima in the molecular lowerings were observed, the following salts being exceptions; rubidium chloride, potassium chloride, lithium chloride, aluminium bromide, potassium sulphocyanate, potassium cyanide, potassium bromide and lithium iodide.

In all of these investigations the observations were confined to comparatively dilute solutions; in no case did the concentrations have a wider range than from extreme dilution to $\frac{3}{2}$ normal. It seemed

[1] Am. Chem. Jour., 23, 512, 1900.

[2] Ztschr. phys. Chem., 40, 185.

very desirable to extend this work to solutions of greater concentration and, to study in this way a large number of different substances.

OBJECT OF THIS INVESTIGATION.

The object of this investigation as already stated, is to extend the work in this field by studying solutions of greater concentration, especially by means of the freezing-point and conductivity methods. By applying these methods to a large number of substances differing widely in chemical and physical properties, it seemed probable that some light might be thrown upon the problems presented by concentrated solutions, and that through such studies we may come to understand why the laws which obtain for dilute solutions fail completely when applied to solutions of greater concentration.

APPARATUS.

Freezing-Point Apparatus.

The accompanying figure (1) shows the apparatus used in determining the freezing-points of the solutions. It will be seen to be essentially that devised by Beckmann. The thermometers used were made expressly for this work. They were of the Beckman type, one having a range of *twelve degrees*, each degree being divided into fiftieths, the other having a range of *twenty-five degrees*, each degree being divided into twentieths. The thermometer with the greater range was employed when working with very concentrated solutions, which gave a large depression, while the more finely divided instrument was used with the more dilute solutions.

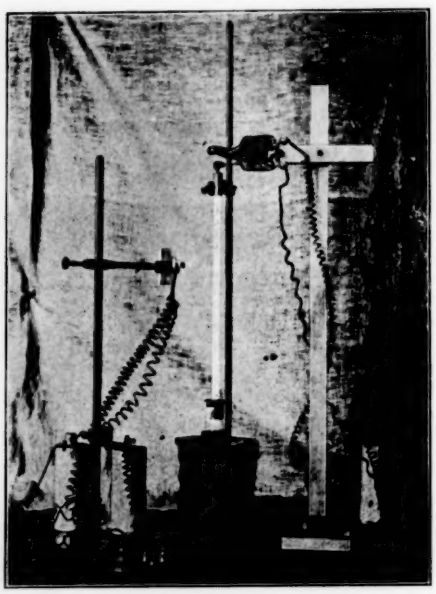


Fig. 1.

The stirrer in the freezing tube consisted of a ring of stout platinum wire around which was wrapped a spiral of fine platinum wire. The size of the ring was such that when wrapped with the smaller wire it would just touch the walls of the freezing tube and thus hinder the formation of an ice-sheath. This device was found to give perfect satisfaction, and to be in every sense superior to the ordinary glass stirrer. The platinum stirrer was attached to a glass rod which passed closely through a glass tube in the cork of the freezing tube. In this way the movement of the stirrer was guided and cramping prevented. The freezing tube consisted of a large test-tube of 80 c.c. capacity. The freezing tube was surrounded by a second glass tube giving an air space between the two of about a centimeter.

This outer tube was surrounded by the freezing mixture, which was contained in a large battery-jar wrapped with felt to prevent radiation.

The freezing mixture was varied to suit the conditions; the solutions of lower concentrations freezing with a mixture of salt and ice, while those of great concentrations often required the use of crystallized calcium chloride and ice.

By means of a small electric hammer uniform and gentle blows were delivered on the top of the thermometer during the time of an observation, thus overcoming the friction of the mercury in the capillary.

To facilitate the reading of the thermometer a small lens magnifying several diameters was employed, and more intense illumination of the thermometer scale was obtained by means of a small incandescent lamp. A thermometer graduated to tenths served to indicate the temperature of the freezing-mixture, the effort being made to keep this only a few degrees lower than the freezing temperature of the solution under observation.

Conductivity Apparatus.

The conductivity measurements were made by the well-known Kohlrausch method using the Wheatstone bridge, inductorium and telephone. Two types of cells were used. For the more dilute solutions the ordinary Arrhenius cell was employed, but for the

very concentrated solutions a specially designed cell was employed. The accompanying sketch (Fig. 2) shows this cell in section.

The U-tube *AA* is 8 cm. in length and 2.8 cm. in diameter. The ground stoppers *BB* are filled with paraffine which serves to hold the tubes *cc* rigidly in place, thus insuring a constant distance between the electrodes. Each stopper is numbered corresponding to a number placed on the ends of the U-tube, so that the electrodes would not be interchanged. Furthermore, by means of fine vertical lines cut on each stopper and the necks of the U-tube, the electrodes could be returned to exactly the same positions each time. That there was no alteration in the distance between the electrodes was carefully established by a series of determinations of the cell constant on successive days, with the result that the differences were well within the limit of experimental error. The electrodes are of thick sheet platinum, and are 2.5 cm. in diameter.

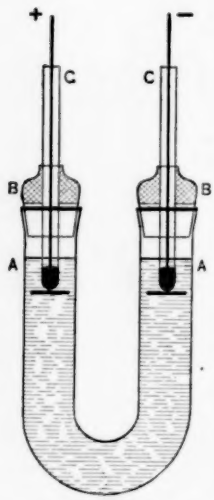


Fig. 2.

All of the conductivity measurements were made at 0°. The bath by which the solutions were maintained at this temperature was prepared in the following manner:

A glass battery-jar was filled with finely crushed, pure ice, to which was added a small volume of water. This jar was placed in a large water-bath, and the space between was packed with well-crushed ice. By this means it was found easy to maintain the solution in the conductivity cell to within one-tenth of a degree of the true zero. The ice in the battery jar was stirred occasionally, and the temperature of the bath was noted frequently, to insure the measurements being taken at 0.

At a later stage of the work it seemed very desirable to supplement the freezing-point and conductivity measurements with determinations of the boiling-point elevations and the refractive indices of some of the solutions. For the former determinations the boiling-point apparatus devised by Jones[1] was employed, while for the refraction measurements use was made of the well-known Pulfrich Refractometer.

[1] Amer. Chem. Journ., 19, 581, 1897.

With the exception of the pipettes the volumetric apparatus used was specially made and carefully calibrated for this investigation.

The volumetric apparatus employed consisted of a series of measuring flasks and a burette and a series of pipettes. The pipettes were never used in making the dilutions.

Solutions.

The method of preparing the solutions varied somewhat according to the substance employed, but, in general, it may be said that a solution of two or three gram-molecular weights to the liter was first made, and from this, by successive dilutions, the less concentrated solutions were obtained. Wherever possible the mother-solution was made up by direct weighing. When this was not the case the solution was standardized either by gravimetric or volumetric methods.

Great care was taken to insure the accurate standardization of the mother-solution, and the dilutions were made with volumes large enough to minimize errors in burette readings and flask adjustments.

The water which was used as a solvent was of a high degree of purity. The ordinary tap-water was first distilled in the laboratory still, and then redistilled from a dilute solution of chromic acid. This second distillate was then distilled a third time according to the method of Jones and Mackay.[1] The water thus obtained was preserved in a large bottle which had previously been subjected to most careful cleaning. The water showed an average conductivity of 2.0×10^{-6}.

Methods.

Freezing-point Method.

The practical details of the freezing-point method may be set forth most clearly by a description of the determination of the freezing-point of water, by which the zero-point of the thermometer was established prior to making any measurements upon solutions.

The freezing-tube was filled to a depth of 5 cm. with pure distilled water, and the thermometer and stirrer inserted. The tube was then placed in a vessel containing ice and salt, and the stirrer agitated frequently until ice separated. The tube was then removed

[1] Amer. Chem. Journ., 19, 83, 1897.

and warmed until the ice just melted. It was then placed in the freezing-jacket, which was surrounded with finely-crushed dry ice to which has been added just enough salt to bring the temperature of the mixture to a few degrees below the freezing point of the solvent, in this case zero.

The stirrer was agitated from time to time until freezing began, when the stirring was continued vigorously, and at the same time the electrical hammer was set in action. The thermometer scale was illumined by the incandescent lamp and the reading taken after the mercury column had remained stationary for about thirty seconds. It was almost always noticed that the solvent undercooled several degrees, and it was frequently necessary to add a small fragment of ice to induce freezing.

In the case of solutions the tendency to undercool was not so marked. Owing to the change in concentration due to the separation of ice, a correction was introduced. The determination of the freezing-point of the solvent as well as of any solution was repeated several times, and the mean of these results taken as the true freezing-point.

CONDUCTIVITY METHOD.

The solution was introduced into the conductivity cell, care being taken to avoid the collection of air bubbles on the electrodes, and the cell was then placed in the zero bath where it was allowed to remain for half an hour; this having been found to be sufficient time for the solution to acquire the uniform temperature of zero degrees. The conductivity was then determined by the well-known Kohlrausch method.

In the more concentrated solutions it was not found necessary to introduce a correction for the slight conductivity of the water.

BOILING-POINT METHOD.

Care was taken to use this method only on days when the barometer remained quite constant. The general method of carrying out a boiling-point measurement was employed, care being taken that the solutions boiled evenly, and that the thermometer was gently tapped before reading.

The boiling-point as recorded is in the mean of a series of readings taken at intervals of thirty seconds, and with each determination is recorded the corresponding barometric height.

Refractivity Method.

The determination of refractive indices was made with the refractometer of Pulfrich. Sodium light was employed and care was taken to have the solutions at uniform temperature. The readings were made to minutes of arc, and by means of the well-known formula $n = \sqrt{N^2 - \sin^2 X}$. The indices of refraction were calculated.

Sources of Error.

In order to freeze solutions of relatively great concentrations it was found necessary to do away with the extra jackets used in working with dilute solutions. This source of error became manifest when the attempt was made to determine the freezing-points of solutions having concentrations less than half normal. This error diminishes as the concentration increases.

It was further found to be quite impossible to use more than 30 c.c. of solution; this limitation introducing another small source of error. The difficulty experienced in keeping at a minimum the difference between the temperature of the freezing-mixture and the freezing temperature of the solution was at times not slight. This was particularly noticeable when calcium chloride was used in the place of salt.

The correction introduced for the increase in concentration due to the separation of ice was the cause of some error. The amount of ice formed being a function of the degree of undercooling, it has been found practicable in working with dilute solutions to apply the correction formula $k = su/w$ to the observed depression.

In this formula s is the specific heat of the liquid, u the undercooling observed and w the latent heat of fusion of the solvent. The solution continues to lose heat even after freezing commences, and the heat lost is therefore greater than that measured by the undercooling, and the latent heat of fusion is less for a concentrated solution than for the pure solvent, so that for a given degree of undercooling there results a greater formation of ice than would result with the pure solvent.

This point has been tested experimentally by Loomis[1] while working with a 0.2 normal solution of sodium chloride. Applying the correction-formula his solution appeared concentrated about 0.2 per cent., whereas by actual determination of the change in concentration he found it to be concentrated 0.3 per cent. Such an error would be increased when the formula is applied to solutions varying from normal to three times normal. Furthermore, the amount of undercooling is found to vary greatly with the same solution upon successive freezings. It has been observed with almost every solution that the degree of undercooling is governed by the amount of over-warming. This same point was observed by Loomis.[2] He says: "Thus, one may effect almost any desired amount of overcooling by properly varying the degree of overwarming." Furthermore, as is well known, freezing can be induced by the introduction of a minute fragment of ice. Thus, it is evident that through this two-fold means of control of the degree of undercooling, some bias might be given to the results. The effort was made to avoid producing this error in the results. It must be stated, however, that this correction term is not entirely satisfactory, and that through its use some slight error has necessarily been introduced.

As has been stated two thermometers were employed in this investigation. One of these was graduated to fiftieths, while the other was divided into twentieths of a degree.

Estimation to hundredths of a degree was, therefore, the closest approximation that could be obtained.

The zero of the thermometer was determined just before making any measurements with the solutions.

The errors in the conductivity measurements were so slight that no record of them need be made. The refractivity measurements are affected by a slight error due to small inequalities of temperature throughout a series of determinations. This, while in general small, manifests itself in one or two of the curves to a noticeable extent.

The boiling-point method contains several sources of error. The platinum cylinder surrounding the thermometer bulb was found to

[1] Loomis, PHYS. REV., 1, 283, 1893.
[2] Loomis, PHYS. REV., 1, 283, 1893.

cause some irregularity in the boiling-point of a concentrated solution, but to remove the cylinder introduces a two-fold error due to radiation and the cooled recondensed solvent.

Furthermore, the extremely low boiling-point constant for water renders the accuracy of the method in the more dilute solutions not very great. Of course the changes in barometric pressure also increase the difficulties in making an accurate boiling-point determination. This latter difficulty, it may be remarked, is greater in this locality than on the continent of Europe, where the barometric pressure remains practically constant for hours. The method gave so much trouble that it was temporarily discarded as being incapable of throwing much light on the problem in hand.

Tabulation of Results.

In the tables of freezing-point measurements the symbols employed have the following significance :

m = concentration in gram-molecular normal.

s = observed freezing-point depression.

k = correction for change in concentration due to separation of ice.

Δ = corrected freezing-point depression.

Δ/m = molecular freezing-point depression.

Wherever possible the results of other observers in the region of greater dilution are given, since, as has been stated, the method employed for concentrated solutions does not give highly accurate results when applied to dilute solutions.

In the tables of boiling-point measurements :

m = molecular concentration.

Δ' = rise of boiling-point.

In the tables of conductivity measurements v denotes the volume and μv the molecular conductivity at 0° C. In the tables of refractivity measurements the notation has the following meaning :

m = concentration in gram-molecular normal.

X = observed angle.

n = index of refraction.

The results are all expressed in curves (Figs. 3–13).

Hydrochloric Acid, HCl (36.46).

The hydrochloric acid used was found to be free from impurities. A solution of approximately three normal concentration was made up by means of the hydrometer. Its exact strength was then determined by diluting an appreciable volume one hundred times, and titrating successive portions by means of potassium hydroxide. The potassium hydroxide solution used had been carefully standardized against sulphuric acid, which, in turn, had been standardized gravimetrically by precipitation as barium sulphate. From the data thus obtained the mother-solution was diluted with the proper volume of water to make it exactly three times normal, and this dilution was then checked by a series of titrations.

From the mother-solution a series of dilutions were made, thus giving the solutions required. It may be well to state that these diluted solutions were preserved in hard-glass bottles, which had been thoroughly cleaned and steamed.

Freezing-point Measurements.

	Δ/m			
m	Loomis.[1]	Jones.[2]	Barnes.[3]	Chambers & Frazer.[4]
0.05	3.594		3.593	3.630
0.10	3.546	3.554	3.565	3.460
0.20	3.565		3.584	3.650
0.30	3.612			
0.40				3.760

m	s	k	Δ	Δ/m
1.0	4.140	0.018	4.122	4.122
1.5	6.720	0.087	6.633	4.422
2.0	10.218	0.281	9.937	4.969
2.5	13.510	0.055	13.455	5.382
3.0	18.100	0.004	18.096	6.030

Conductivity Measurements.

v.	2.000	1.000	0.667	0.500	0.400	0.333
μv.	216.50	200.32	182.35	170.19	152.38	141.87

[1] PHYS. REV., 3, 276, 1896.
[2] Zeit. Phys. Chem., 12, 628, 1893.
[3] Trans. Roy. Soc. Can., Vol. VI., Sec. 50.
[4] Am. Chem. Jour. 23, 515, 1900.

Lithium Chloride, LiCl (42.48).

The concentration of the mother-solution of lithium chloride was determined volumetrically by means of a standard solution of silver nitrate.

The dilutions were made in the usual manner.

Owing to the limited supply of this salt it was impossible to carry the determinations beyond normal concentration.

Freezing-point Measurements.

m	s	k	Δ	Δ/m
0.06	0.250	0.010	0.240	4.067
0.12	0.450	0.010	0.440	3.667
0.24	0.865	0.003	0.862	3.592
0.59	2.245	0.003	2.242	3.800
1.18	4.800	0.001	4.799	4.066

Conductivity Measurements.

$v.$	16.95	8.47	4.22	1.67	0.88
$\mu v.$	53.75	50.42	46.76	42.28	35.58

Refractivity Measurements.

m	X	n
0.06	67° 22′	1.32438
0.12	67 16	1.32585
0.24	67 —	1.32711
0.59	66 21	1.33021
1.18	65 19	1.33526

Boiling-point Measurements.[1]

m	Δ'	Barom. Press.	Δ'/m
0.0135	0.130	Constant.	0.960
0.2584	0.245		0.950
0.5899	0.568		0.963
1.0500	1.063		1.010
1.6240	1.743		1.070

Ammonium Chloride, NH_4Cl (53.53).

The salt used was dried for several days in a desiccator over phosphorus pentoxide.

[1] Biltz. Ztschr. phys. Chem., 40, 208, 1902.

The $3N$, $2N$ and N solutions were made up by direct weighing. The less concentrated solutions were made by diluting the normal solution. This method was pursued to avoid weighing such large masses of salt.

Freezing-point Measurements.

	Δ/m			
m	Loomis.[1]		Biltz.[2]	
0.04	3.50		3.39	
0.05	3.48			
0.10	3.434			
0.20	3.396			
0.26			3.39	
0.40	3.393			
0.54			3.41	
m	s	k	Δ	Δ/m
1.0	3.75	0.020	3.730	3.730
2.0	7.55		7.550	3.775
3.0	11.70		11.700	3.900

Conductivity Measurements.

$v.$	5.0	2.0	1.0	0.5	0.333
$\mu v.$	68.94	66.15	64.35	59.27	58.61

Refractivity Measurements.

m	X	n
0.2	66° 55′	1.32750
0.5	66 18	1.33045
1.0	65 15	1.33559
2.0	63 20	1.34536
3.0	61 30	1.35508

Sodium Chloride, NaCl (58.50).

The sodium chloride used was prepared from ordinary salt by precipitation from concentrated solution by means of hydrochloric acid gas. The salt thus obtained was washed with a little cold water, and was then dried at 120° C in an air bath.

The 3N, 2N and N solutions were made up by direct weighing, the latter serving as the mother-solution for the lesser concentrations.

[1] PHYS. REV., 3, 276, 1896.
[2] Ztschr. Phys. Chem., 40, 198, 1902.

Freezing-point Measurements.

	Δ/m			
m	Loomis.[1]	Jones.[2]	Biltz.[3]	Kahlenberg.[4]
0.05	3.531	3.52	3.41	—
0.06	3.529	—	—	—
0.07	3.510	—	—	—
0.08	3.501	—	—	—
0.09	3.494	—	—	—
0.10	3.484	3.47	3.47	3.26
0.20	3.439	3.42	3.44	—
0.26	—	—	—	3.19
0.30	—	—	—	3.21
0.40	—	—	3.42	—
0.50	—	—	—	3.24

m	s	k	Δ	Δ/m
0.5	1.760	0.001	1.759	3.518
1.0	3.550	0.004	3.546	3.546
2.0	7.470	0.003	7.467	3.734
3.0	12.225	0.002	12.223	4.074

Conductivity Measurements.

$v.$	5.000	2.000	1.000	0.500	0.333
$\mu v.$	51.84	48.62	47.16	43.14	36.59

Refractivity Measurements.

m	X	n
0.2	67° 1′	1.32703
0.5	66 24	1.32997
1.0	65 26	1.33469
2.0	63 37	1.34389
3.0	61 59	1.35249

Boiling-point Measurements.[5]

m	Δ'	Barom. Press.	Δ'/m
0.1256	0.195	754.0 mm.	1.552
0.2500	0.390	"	1.160
0.3793	0.598	"	1.576
0.5046	0.820	"	1.625
0.6299	1.031	"	1.637
0.8792	1.474	"	1.677
1.1409	1.970	"	1.726
2.0130	4.471	743.5	2.221
3.1242	6.820	743.4	2.183

[1] PHYS. REV., I., 279, 1893. [2] Zeit. Phys. Chem., 11, 110, 1893.
[3] Ibid., 40, 199, 1902. [4] Jour. Phys. Chem., 5, 353, 1901.
[5] Kahlenberg, Jour. Phys. Chem., 5, 362, 1901.

Potassium Chloride, KCl (74.60).

The salt used was prepared by repeated crystallization from fairly pure specimens. It was then dried for several days in an air-bath at 110° C. and afterwards preserved in a desiccator over calcium chloride until it was used.

From the mother-solution prepared by direct weighing, the lesser concentrations were obtained by dilution.

Freezing-point Measurements.

	Δ/m		
m	Loomis[1].	Jones.[2]	Biltz.[3]
0.05	3.50	3.50	——
0.10	3.445	3.47	3.47
0.20	3.404	——	——
0.30	——	——	3.41
0.40	3.353	——	——
0.50	——	——	3.34
0.80	——	——	3.27

m	s	k	Δ	Δ/m
0.2	0.688	0.003	0.685	3.425
0.5	1.695	0.003	0.692	3.384
1.0	3.400	——	3.400	3.400
2.0	6.950	0.006	6.944	3.472
3.0	11.065	0.003	11.062	3.687

Conductivity Measurements.

$v.$	20.0	10.0	5.0	2.0	1.0	0.5
$\mu v.$	72.37	69.53	68.71	65.21	61.07	60.98

Boiling-point Measurements.[4]

m	Δ'	Barom. Press.	Δ'/m
0.2122	0.293	737.6 mm.	1.381
0.5124	0.700	"	1.366
0.9012	1.247	"	1.383
1.3990	2.004	"	1.432
2.0170	2.975	"	1.475
2.4160	3.653	"	1.512
2.7720	4.266	"	1.539
3.1840	5.009	"	1.570

[1] PHYS. REV., 3, 276, 1896.
[2] Ztschr. phys. Chem., 11, 110, 1893.
[3] Ibid., 40, 198, 1902.
[4] Kahlenberg, Jour. Phys. Chem., 5, 363, 1901.

Calcium Chloride, $CaCl_2$ (110.8).

The salt was obtained in a well-crystallized condition. It was dissolved in enough water to insure the solution having a concentration of at least 2.5N. By means of several gravimetric determinations of calcium the exact strength of the mother-solution was obtained. It was then diluted to 2.5N and the calcium redetermined as a check. From this mother-solution the other solutions were prepared by dilution.

It may be noted at this point that owing to the extremely large depressions produced by concentrated solutions of this substance, it was necessary to employ crystallized calcium chloride and ice as the freezing mixture.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones & Chambers.[2]
0.05	4.85	
0.10	4.80	4.98
0.20	4.84	4.96
0.30		5.02
0.40		5.16
0.50	5.19	5.26

m	s	k	Δ	Δ/m
1.0	6.350	0.005	6.345	6.345
1.5	11.300	0.004	11.296	7.531
2.0	17.875	0.008	17.867	8.934

Conductivity Measurements.

v.	1.000	0.667	0.500	0.400
μv.	71.16	62.14	53.98	44.79

Strontium Chloride, $SrCl_2$ (158.5).

The salt was purified by repeated crystallizations, and finally dried at 110° C. It was preserved in a desiccator over calcium chloride until used.

The mother-solution was made up by direct weighing, and then analyzed for both strontium and chlorine as a check. The dilutions were made in the usual manner.

[1] PHYS. REV., 4, 298, 1897.
[2] Amer. Chem. Jour., 23, 93, 1900.

Freezing-point Measurements.

	Δ/m			
m	Loomis.[1]		Jones & Chambers.[2]	
0.05	4.90		5.16	
0.10	4.85		4.88	
0.20	4.82		4.87	
0.30			4.90	
0.40			4.95	
0.50	5.08		5.09	
m	s	k	Δ	Δ/m
1.0	6.010	0.010	6.000	6.000
1.5	10.725		10.725	7.150
2.0	16.425	0.003	16.422	8.211

Conductivity Measurements.

v.	2.000	1.000	0.667	0.500
μv.	84.26	74.57	63.01	55.26

Barium Chloride, $BaCl_2$ (208.3).

The salt was obtained in a relatively pure condition. It was recrystallized several times, and then dried for some hours at 110° C. in the air-bath.

The mother-solution was made up by direct weighing and the lesser concentrations obtained by dilution. The slight solubility of the salt prevented the study of concentrations beyond 0.75N.

Freezing-Point Measurements.

	Δ/m			
m	Loomis.[3]		Jones & Chambers.[4]	
0.05	4.770			
0.10	4.690		4.85	
0.20	4.655		4.77	
0.30			4.82	
0.50	4.830		4.95	
m	s	k	Δ	Δ/m
0.5	2.500	0.007	2.493	4.986
0.75	3.860	0.003	3.857	5.143

Conductivity Measurements.

v	20.000	10.000	4.000	2.000	1.333
μv	116.05	103.79	95.94	89.24	85.27

[1] PHYS. REV., 4, 287, 1897. [2] Amer. Chem. Jour., 23, 94, 1902.
[3] PHYS. REV., 3, 277, 1896. [4] Amer. Chem. Jour., 23, 94, 1900.

Boiling-point Measurements.[1]

m	Δ'	Barom. Press.	Δ'/m
0.3397	0.208	752.8 mm.	0.612
0.8290	0.496	"	0.598
1.3612	0.839	"	0.616
1.9868	1.293	"	0.651
2.7071	1.909	"	0.705
3.5036	2.517	"	0.718

Nitric Acid, HNO_3 (63.05).

By means of the hydrometer and Lunge's tables a solution of approximately 3N was made up. This solution was then accurately standardized by means of potassium hydroxide, the same method being used as in the case of hydrochloric acid.

From the mother-solution thus prepared, the more dilute solutions were obtained.

Freezing point Measurements.

	Δ/m			
m	Jones.[2]		Loomis.[3]	
0.05	3.71		3.51	
0.10	3.53		3.50	
0.20			3.48	
m	s	k	Δ	Δ/m
0.5	1.840	0.018	1.822	3.644
1.0	3.850	0.054	3.796	3.796
1.5	5.980	0.042	5.938	3.959
2.0	8.425	0.015	8.410	4.205
2.5	11.125	0.079	11.046	4.418
3.0	14.058	0.150	13.908	4.636

Conductivity Measurements.

$v.$	2.000	1.000	0.667	0.500	0.400	0.333
$\mu v.$	213.30	194.95	184.89	169.23	155.43	140.97

Lithium Nitrate, $LiNO_3$ (69.07).

The sample of lithium nitrate used was obtained in well-crystallized form. It was heated to 120° C. for several days in an air-bath, and was then allowed to cool in a desiccator over calcium chloride. When cool, the mother-solution was prepared by direct

[1] Kahlenberg, Jour. Phys. Chem., 5, 366, 1901.
[2] Zeit. Phys. Chem., 12, 623, 1893.
[3] PHYS. REV. 4, 282, 1897.

weighing of the salt, care being taken to make the weighing as quickly as possible after the removal of the salt from the desiccator.

Owing to the limited supply of this salt the mother-solution contained only one gram-molecule of dissolved substance in a liter.

Freezing-point Measurements.

m	s	k	Δ	Δ/m
0.05	0.185	0.002	0.183	3.660
0.10	0.355	0.002	0.353	3.530
0.20	0.745	0.023	0.722	3.610
0.30	1.095	0.001	1.094	3.647
0.40	1.465	0.003	1.462	3.655
0.50	1.860	0.005	1.855	3.710
0.60	2.275	0.008	2.267	3.778
0.70	2.665	0.002	2.663	3.804
0.80	3.135		3.135	3.919
0.90	3.560	0.003	3.557	3.952

Conductivity Measurements.

$v.$	20.00	10.00	5.00	3.33	2.50	2.00	1.67	1.43	1.25	1.11
$\mu v.$	50.00	47.56	45.91	44.05	43.90	42.50	40.81	39.91	39.89	37.74

Ammonium Nitrate, NH_4NO_3 (80.12).

The salt was obtained in a comparatively pure condition, and was recrystallized several times. It was then dried at 100° C. and preserved until needed in a desiccator over calcium chloride.

The mother-solution was prepared by direct weighing, and from it the successive dilutions were made.

Freezing-point Measurements.

	Δ/m
m	Loomis.[1]
0.025	3.49
0.050	3.47
0.100	3.424
0.200	3.321

m	s	k	Δ	Δ/m
0.5	1.690	0.004	1.686	3.372
1.0	3.150	0.005	3.145	3.148
2.0	6.000	0.004	5.996	2.998
3.0	8.725	0.005	8.720	2.906

[1] PHYS. REV., 3, 279, 1896.

Conductivity Measurements.

$v.$	20.0	10.0	5.0	2.0	1.0	0.5
$\mu v.$	67.49	65.05	63.44	60.26	54.97	52.81

Refractivity Measurements.

m	X	n
0.05	67° 22′	1.32538
0.10	67 21	1.32585
0.20	67 3	1.32687
0.50	66 25	1.32989
1.00	65 24	1.33485
2.00	63 30	1.34449

Sodium Nitrate, $NaNO_3$ (85.09).

The sample of sodium nitrate used was purified by repeated crystallizations. The purified salt was dried at 110° C. in an air-bath, and preserved over calcium chloride in a desiccator until required.

The mother-solution was made up by direct weighing, and the other solutions obtained from this by dilution.

Freezing-Point Measurements.

	Δ/m
m	Loomis.[1]
0.05	3.44
0.10	3.428
0.20	3.345

m	s	k	Δ	Δ/m
1.0	3.200	0.002	3.198	3.198
1.5	4.670	0.001	4.669	3.113
2.0	6.150	0.003	6.147	3.074
2.5	7.470	0.002	7.468	2.987
3.0	8.913	0.004	8.909	2.969

Conductivity Measurements.

$v.$	2.000	1.000	0.667	0.500	0.400
$\mu v.$	44.90	40.41	36.90	34.16	30.96

Potassium Nitrate, KNO_3 (101.19).

The specimen of potassium nitrate was obtained in a fair state of purity. This was recrystallized until it no longer gave a flame-test for sodium. It was then dried for several days at 110° C. in

[1] PHYS. REV., 3, 279, 1896.

an air-bath, after which it was preserved in a desiccator over calcium chloride until required for use.

The mother-solution was made up by direct weighing, and the remaining solutions made by dilution.

Freezing-point Measurements.

	Δ/m
m	Loomis.[1]
0.05	3.41
0.10	3.314
0.20	3.194

m	s	k	Δ	Δ/m
0.4	1.295	0.037	1.258	3.145
0.5	1.553	0.016	1.537	3.074
1.0	2.730	0.001	2.729	2.729

Conductivity Measurements.

$v.$	2.000	1.000	0.667
$\mu v.$	53.20	49.97	46.30

Boiling-point Measurements.[2]

m	Δ'	Barom. Press.	Δ'/m
0.2789	0.248	741.1 mm.	0.889
0.6058	0.518	"	0.855
0.9721	0.822	"	0.845
1.4798	1.207	"	0.815
2.1333	1.706	741.2	0.795
2.7095	2.123	"	0.783

Sulphuric Acid, H_2SO_4 (98.08).

The acid used was free from the ordinary impurities.

By means of the hydrometer and Lunge's tables a solution approximately 3N was made up. A portion of this solution was then diluted a hundred times, and successive portions of this diluted solution were removed for titration with N/5 potassium hydroxide. After the exact strength of the solution was ascertained, it was diluted sufficiently to make the solution strictly 3N.

[1] PHYS. REV., 3, 278, 1896.

[2] Kahlenberg, Jour. Phys. Chem., 5, 368, 1901.

This solution was then checked by several titrations. As has been said the potassium hydroxide solution used for the titration was standardized by means of N/5 sulphuric acid, which had been standardized gravimetrically.

The dilutions were made as usual from the mother-solution.

Freezing-point Measurements.

	Δ/m			
m	Loomis.[1]	Jones.[2]		Barnes.[3]
0.05	4.130			4.167
0.10	3.968	3.945		3.961
0.20	3.850			3.883
m	s	k	Δ'	Δ/m
0.10	0.413	0.016	0.397	3.970
0.30	1.180	0.024	1.156	3.853
0.50	2.040	0.023	2.017	4.034
1.00	4.203	0.014	4.189	4.189
1.50	7.450	0.007	7.443	4.962
2.00	11.300	0.004	11.296	5.648
2.50	16.275		16.275	6.510

Conductivity Measurements.

$v.$	2.000	1.000	0.667	0.500	0.400	0.333	0.286	0.250	0.222	0.200
$\mu v.$	277.30	253.44	221.25	199.42	178.79	155.29	135.00	118.86	100.21	86.97

Ammonium Sulphate, $(NH)_2SO_4$ (*114.14*).

The salt used was purified by several recrystallizations. It was dried at 100° C. in an air-bath, and was then preserved in vacuo over sulphuric acid until required.

The mother-solution was made up by direct weighing, and the lesser concentrations obtained by dilution.

Freezing-point Measurements.

m	s	k		$/m$
0.05	0.025	0.001	0.024	4.80
0.10	0.475	0.006	0.469	4.69
0.20	0.825	0.007	0.818	4.09
0.50	1.975	0.006	1.969	3.94
1.00	3.725	0.039	3.686	3.69
1.40	5.200	0.067	5.133	3.67

[1] PHYS. REV., I., 281, 1893. [2] Ztschr. phys. Chem., 12, 628, 1893.
[3] Trans. Roy. Soc. Canada, Vol. VI., Sec. III., 50.

Conductivity Measurements.

$v.$	20	10	5	2	1	0.71
$\mu v.$	100.60	95.84	86.15	80.08	72.55	69.30

Refractivity Measurements.

m	X	n
0.05	67° 15′	1.32593
0.10	67	1.32711
0.20	66 45	1.32829
0.50	65 42	1.33338
1.00	64 7	1.34131
1.40	62 49	1.34807

Sodium Sulphate, Na_2SO_4 (142.16).

The salt used was in the form of the decahydrate.

It was heated to 120° C. for several days, and was then removed from the air bath and finely pulverized in a mortar, after

Freezing-point Measurements.

	Δ/m
m	Loomis.[1]
0.05	4.590
0.10	4.340
0.20	4.071
0.30	3.875

m	s	k	Δ	Δ/m
0.50	1.850	0.011	1.839	3.678

Conductivity Measurements.

$v.$	20.0	10.00	5.00	2.00	1.00	0.67	0.50
$\mu v.$	93.06	84.92	73.09	60.54	47.13	36.82	28.54

Refractivity Measurements.

m	X	n
0.05	67° 13′	1.32609
0.10	66 58	1.32727
0.20	66 30	1.32949
0.50	65 20	1.33518
1.00	63 37	1.34389
1.50	62 05	1.35195
2.00	60 43	1.35934

[1] PHYS. REV., 3, 277, 1896.

which it was placed over sulphuric acid in a vacuum desiccator until required. The mother-solution was made up by direct weighing.

Owing to the formation of the hydrate upon cooling, it was found impossible to extend the observations on the freezing-point beyond N/2 concntration.

Boiling-point Measurements.

m	Δ'	Barom. Press.	Δ'/m
0.05	0.050	763.0 mm.	1.00
0.10	0.105	763.1	1.05
0.20	0.235	763.3	1.17
0.50	0.531	763.5	1.06
1.00	1.064	763.5	1.06
1.50	1.748	765.0	1.07
2.00	2.085	764.8	1.04

Potassium Sulphate, K_2SO_4 (174.06).

The specimen of salt used was dried for several days in the air-bath at a temperature of 120° C., and was then preserved in a desiccator over sulphuric acid until required.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.05	4.540	4.61
0.10	4.317	4.28
0.20	4.067	
0.30	3.891	

Conductivity Measurements.

$v.$	20	10	5	2
$\mu v.$	118.89	109.79	98.88	88.93

Refractivity Measurements.

m	X	n
0.05	67° 12′	1.32616
0.10	66 57	1.32735
0.20	66 30	1.32949
0.50	65 20	1.33518

[1] PHYS. REV., 3, 277, 1896.

[2] Ztschr. phys. Chem., 11, 527, 1893.

The mother-solution was made up by direct weight.

Owing to the excessively slight solubility of this salt it was impossible to extend the freezing-point observations beyond $\frac{3}{10}$N.

It is also worthy of note at this point that the refractive indices for solutions of sodium and potassium sulphates are nearly identical, as may be seen from the curves.

Sodium Carbonate, Na_2CO_3 (106.1).

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.05	4.640	4.67
0.10	4.416	4.45
0.20	4.170	

m	s	k	Δ	Δ/m
0.5	1.883	0.001	1.882	3.764

Conductivity Measurements.

$v.$	20	10	5	2	1	0.5
$uv.$	85.80	76.80	66.90	53.10	39.14	24.53

Refractivity Measurements.

m	X	n
0.05	67° 14′	1.32601
0.10	66 57	1.32735
0.20	66 29	1.32957
0.50	65 12	1.33584
1.00	63 20	1.34536
2.00	60 13	1.36209

Boiling-point Measurements.

m	Δ'	Barom. Pressure.	Δ'/m
0.05	0.053	763.5 mm.	1.060
0.10	0.132	763.7	1.320
0.20	0.258	763.8	1.290
0.50	0.538	764.3	1.176
1.00	0.947	765.3	0.947
2.00	1.747	771.5	0.874

[1] PHYS. REV., 3, 278, 1896.

[2] Ztschr. phys. Chem., 12, 623, 1893.

The salt was dried for twenty-four hours over sulphuric acid in vacuo. The solutions were made up by direct weighing and dilution. Owing to the separation of the hydrate, freezing-point measurements beyond 0.2N were impossible.

Potassium Carbonate, K_2CO_3 (138.3).

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.05	4.710	4.75
0.06		4.75
0.10	4.540	4.62
0.20	4.385	

m	s	k	Δ	Δ/m
0.4	1.728	0.045	1.683	4.208
1.0	4.383	0.008	4.375	4.375
2.0	9.725	0.015	9.710	4.855

Conductivity Measurements.

$v.$	20	10	5	2.5	1	0.5
$\mu v.$	114.04	104.34	95.54	87.05	74.25	61.57

Refractivity Measurements.

m	X	n
0.05	67° 10′	1.32632
0.10	66 54	1.32758
0.20	66 26	1.32980
0.40	65 35	1.33395
1.00	63 18	1.34553
2.00	60 12	1.36219

Boiling-point Measurements.

m	Δ'	Barom. Press.	Δ'/m
0.05	0.055	765.5 mm.	1.100
0.10	0.102	765.5	1.020
0.20	0.194	765.2	0.970
0.40	0.378	765.0	0.945
1.00	1.080	764.5	1.080
2.00	2.680	764.5	1.340

[1] PHYS. REV., 3, 278, 1896.

[2] Ztschr. phys. Chem., 12, 623, 1893.

The specimen used was dried for six days in vacuo over sulphuric acid. The mother-solution was made up by direct weighing and the lesser concentrations were obtained by dilution.

Phosphoric Acid, H_3PO_4 (98.03).

The acid was obtained in a well-crystallized condition. It was dissolved in pure water and the strength of the solution determined by means of gravimetric analysis, the phosphoric acid being weighed as magnesium pyrophosphate.

The analysis was checked by means of a pyknometric determination of its specific gravity.

Freezing-point Measurements.

	Δ/m			
m	Loomis.[1]		Jones.[2]	
0.05	2.490			
0.06			2.65	
0.10	2.358		2.35	
0.15			2.32	
0.20	2.249			
m	s	k	Δ	Δ/m
0.52	1.138	0.027	1.111	2.137
1.04	2.475	0.007	2.468	2.373
2.08	5.408	0.010	5.398	2.595
3.12	9.463	0.008	9.455	3.030

Conductivity Measurements.

v.	15.39	7.68	3.85	1.92	0.96	0.48	0.32
μv.	82.18	62.06	50.38	42.92	37.70	34.89	33.16

Refractivity Measurements.

m	X	n
0.065	67° 18′	1.32570
0.130	67 12	1.32616
0.260	66 55	1.32750
0.520	66 30	1.32949
1.040	65 39	1.33362
2.080	64 00	1.34191
3.120	62 30	1.34974

[1] PHYS. REV., 3, 279, 1896.
[2] Ztschr. phys. Chem., 12, 623, 1893.

Here, as in all similar cases, care was taken to dilute an appreciable volume of the mother-solution, and to employ a large volume of the diluted solution for the analysis. From the standardized mother-solution the lesser concentrations were obtained by dilution.

Potassium Di-hydrogen Phosphate, KH_2PO_4 (136.17).

The specimen used was dried in an air-bath for three days at 100° C. and was then preserved in vacuo over sulphuric acid. The mother-solution was made up by direct weighing and the lesser concentrations obtained by dilution.

Owing to the slight solubility of the salt it was found to be impossible to extend the freezing-point measurements beyond normal concentration.

Freezing-point Measurements.

	Δ/m				
m	Loomis.[1]				
0.01	3.58				
0.02	3.60				
0.05	3.48				
0.10	3.37				
0.20	3.22				
m	s	k	Δ	Δ/m	
0.5	1.525		1.525	3.050	
1.0	2.800	0.020	2.780	2.780	

Conductivity Measurements.

v.	20.0	10.0	5.0	2.0	1.0	0.667
$v\mu$.	51.00	46.71	42.45	38.24	32.21	26.98

Refractivity Measurements.

m	X	n
0.05	67° 15′	1.32593
0.10	67 00	1.32711
0.20	66 45	1.32829
0.50	65 50	1.33272
1.00	64 25	1.33978
1.50	63 10	1.34623

[1] PHYS. REV., 4, 284, 1897.

The specimen used was dried for six days in vacuo over sulphuric acid. The mother-solution was made up by direct weighing and the lesser concentrations were obtained by dilution.

Phosphoric Acid, H_3PO_4 (98.03).

The acid was obtained in a well-crystallized condition. It was dissolved in pure water and the strength of the solution determined by means of gravimetric analysis, the phosphoric acid being weighed as magnesium pyrophosphate.

The analysis was checked by means of a pyknometric determination of its specific gravity.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.05	2.490	
0.06		2.65
0.10	2.358	2.35
0.15		2.32
0.20	2.249	

m	s	k	Δ	Δ/m
0.52	1.138	0.027	1.111	2.137
1.04	2.475	0.007	2.468	2.373
2.08	5.408	0.010	5.398	2.595
3.12	9.463	0.008	9.455	3.030

Conductivity Measurements.

$v.$	15.39	7.68	3.85	1.92	0.96	0.48	0.32
$\mu v.$	82.18	62.06	50.38	42.92	37.70	34.89	33.16

Refractivity Measurements.

m	X	n
0.065	67° 18′	1.32570
0.130	67 12	1.32616
0.260	66 55	1.32750
0.520	66 30	1.32949
1.040	65 39	1.33362
2.080	64 00	1.34191
3.120	62 30	1.34974

[1] PHYS. REV., 3, 279, 1896.
[2] Ztschr. phys. Chem., 12, 623, 1893.

Here, as in all similar cases, care was taken to dilute an appreciable volume of the mother-solution, and to employ a large volume of the diluted solution for the analysis. From the standardized mother-solution the lesser concentrations were obtained by dilution.

Potassium Di-hydrogen Phosphate, KH_2PO_4 (136.17).

The specimen used was dried in an air-bath for three days at 100° C. and was then preserved in vacuo over sulphuric acid. The mother-solution was made up by direct weighing and the lesser concentrations obtained by dilution.

Owing to the slight solubility of the salt it was found to be impossible to extend the freezing-point measurements beyond normal concentration.

Freezing-point Measurements.

	Δ/m
m	Loomis.[1]
0.01	3.58
0.02	3.60
0.05	3.48
0.10	3.37
0.20	3.22

m	s	k	Δ	Δ/m
0.5	1.525		1.525	3.050
1.0	2.800	0.020	2.780	2.780

Conductivity Measurements.

v.	20.0	10.0	5.0	2.0	1.0	0.667
$v\mu$.	51.00	46.71	42.45	38.24	32.21	26.98

Refractivity Measurements.

m	X	n
0.05	67° 15′	1.32593
0.10	67 00	1.32711
0.20	66 45	1.32829
0.50	65 50	1.33272
1.00	64 25	1.33978
1.50	63 10	1.34623

[1] PHYS. REV., 4, 284, 1897.

Sodium Hydroxide, NaOH (40.06).

The mother-solution of sodium hydroxide was made from a chemically pure specimen. The exact strength of the solution was determined by titration with N/5 sulphuric acid, care being taken to work with volumes sufficiently large to minimize errors in dilution and burette readings. The more dilute solutions were prepared by diluting the mother-solutions. The solutions were used as soon as possible after preparation to avoid error, owing to the solvent action of the alkali on the glass of the containing bottles, and to the absorption of carbon dioxide from the air.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.02	3.46	
0.05	3.45	3.56
0.10	3.41	3.42
0.20	3.41	

m	s	k	Δ	Δ/m
0.52	2.175	0.026	2.149	3.466
1.24	4.492	0.043	4.449	3.588
1.86	7.175	0.036	7.139	3.838
2.48	9.775	0.010	9.765	3.937

Conductivity Measurements.

$v.$	16.0	8.0	2.0	0.81	0.54	0.40
$\mu v.$	117.00	115.00	104.00	93.46	80.08	71.43

Potassium Hydroxide, KOH (56.0).

Chemically pure potassium hydroxide from alcohol was used in the preparation of the mother-solution. The concentration of this original solution was determined by titration with N/5 sulphuric acid, and the dilutions made in the usual manner. The same precautions were taken as with sodium hydroxide, to prevent the solutions from becoming contaminated with silicates and carbonates.

[1] PHYS. REV., 4, 282, 1897.
[2] Ztschr. phys. Chem., 12, 623, 2893.

Freezing-point Measurements.

	Δ/m	
m	Loomis.[1]	Jones.[2]
0.05	3.44	3.58
0.10	3.43	3.47
0.20	3.43	

m	s	k	Δ	Δ/m
0.5	1.810	0.002	1.808	3.616
1.0	3.920	0.039	3.881	3.881
1.5	5.975	0.011	5.964	3.976
2.0	8.492	0.006	8.486	4.243
2.5	11.308	0.006	11.302	4.521

Conductivity measurements.

v.	16.0	8.0	2.0	1.0	0.667	0.500	0.400
μv.	125.30	122.80	118.40	113.33	106.35	101.15	97.40

Fig. 3.

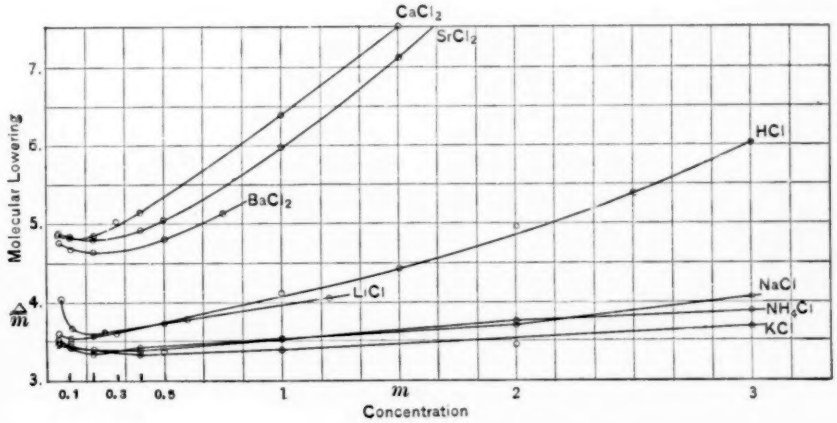
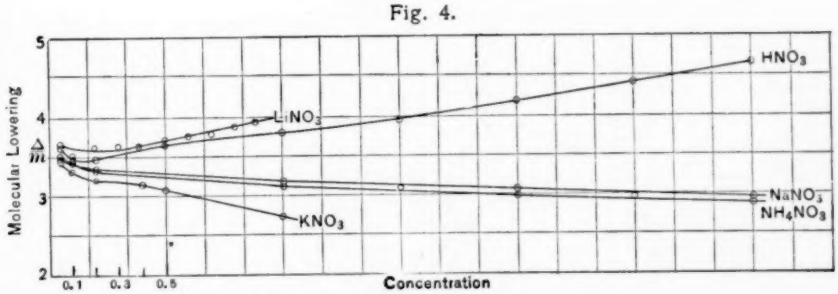


Fig. 4.



[1] PHYS. REV., 4, 282, 1897.

[2] Ztschr. phys. Chem., 12, 623, 1893.

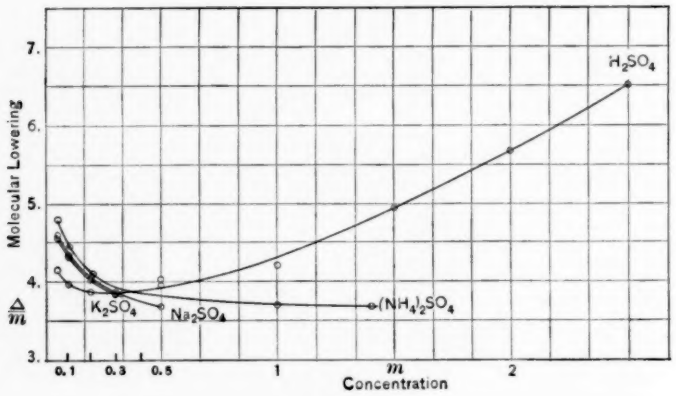
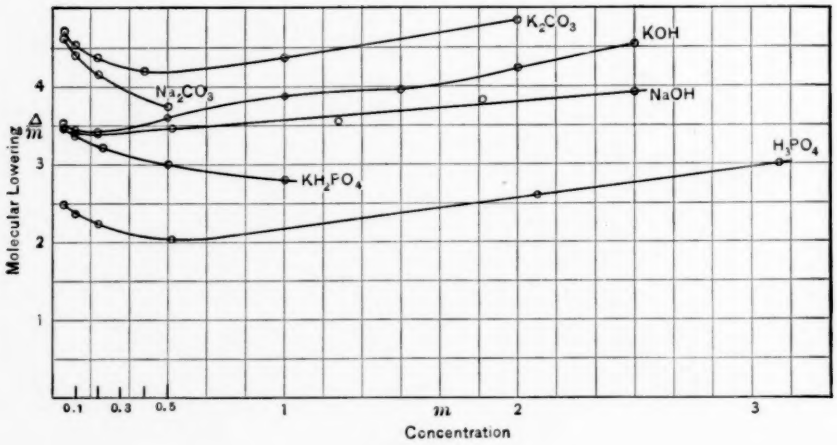

Molecular Lowering
$\frac{\Delta}{m}$
7.
6.
5.
4.
3.
H_2SO_4
K_2SO_4
Na_2SO_4
$(NH_4)_2SO_4$
0.1
0.3
0.5
1
2
m
Concentration

Fig. 5.


Molecular Lowering
$\frac{\Delta}{m}$
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2
1
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KOH
Na_2CO_3
NaOH
H_3PO_4
KH_2PO_4
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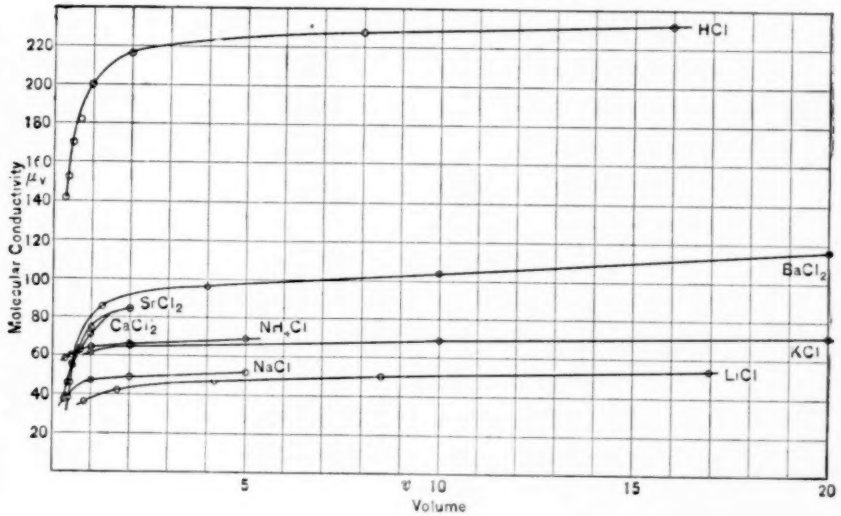
0.3
0.5
1
2
3
m
Concentration

Fig. 6.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BaCl2
SrCl2
CaCl2
NH4Cl
KCl
NaCl
LiCl
Molecular Conductivity
μv
Volume
v
220
200
180
160
140
120
100
80
60
40
20
5
10
15
20

Fig. 7.

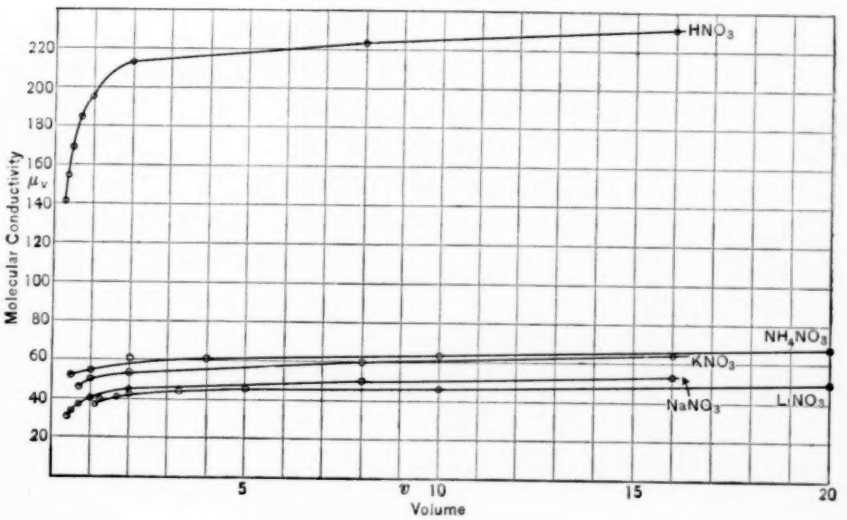
HNO3
NH4NO3
KNO3
NaNO3
LiNO3
Molecular Conductivity
μv
Volume
v
220
200
180
160
140
120
100
80
60
40
20
5
10
15
20

Fig. 8.

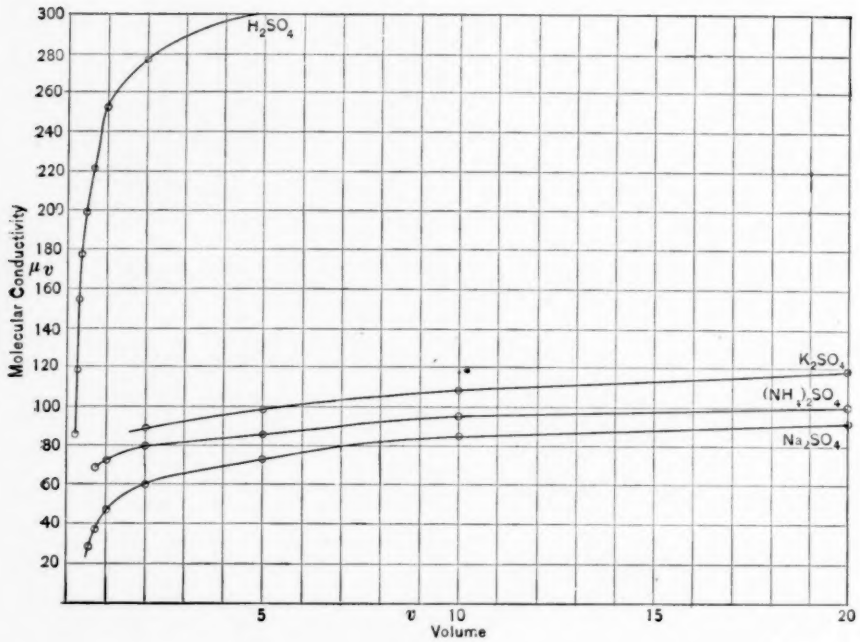
H_2SO_4
K_2SO_4
$(NH_4)_2SO_4$
Na_2SO_4
Molecular Conductivity
μv
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
5
10
15
20
v
Volume

Fig. 9.

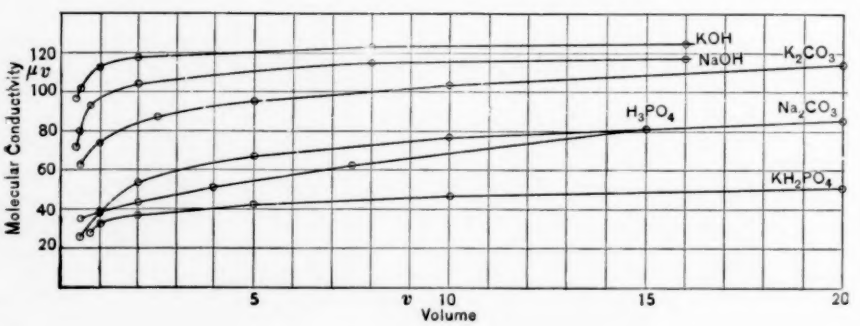
KOH
NaOH
K_2CO_3
H_3PO_4
Na_2CO_3
KH_2PO_4
Molecular Conductivity
μv
120
100
80
60
40
20
5
10
15
20
v
Volume

Fig. 10.

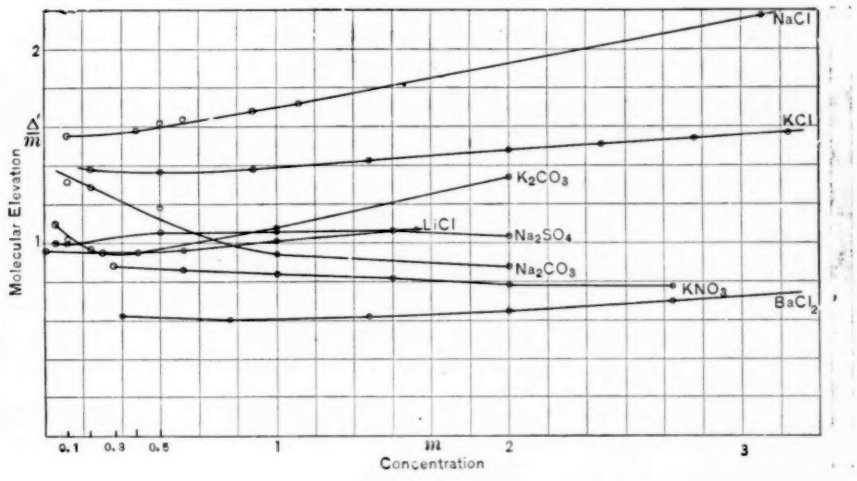
NaCl
KCl
K_2CO_3
LiCl
Na_2SO_4
Na_2CO_3
KNO_3
$BaCl_2$
$\frac{\Delta'}{m}$
Molecular Elevation
2
1
0.1
0.3
0.5
1
m
2
3
Concentration

Fig. 11.

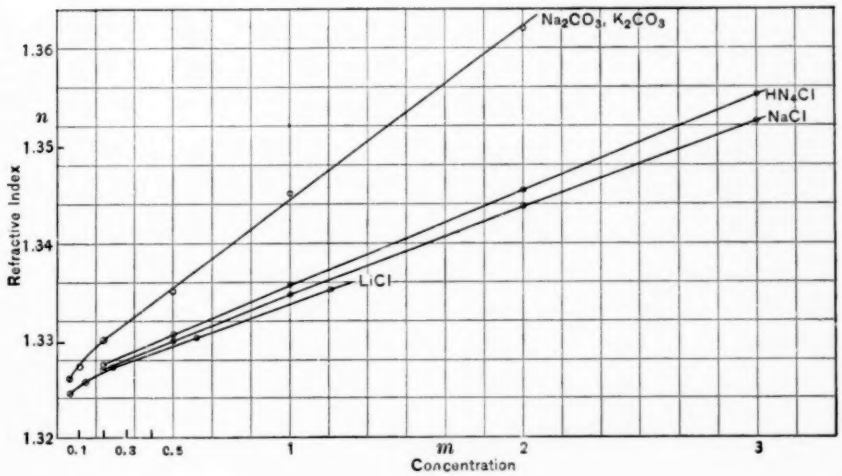
Na_2CO_3, K_2CO_3
HN_4Cl
NaCl
LiCl
n
Refractive Index
1.36
1.35
1.34
1.33
1.32
0.1
0.3
0.5
1
m
2
3
Concentration

Fig. 12.

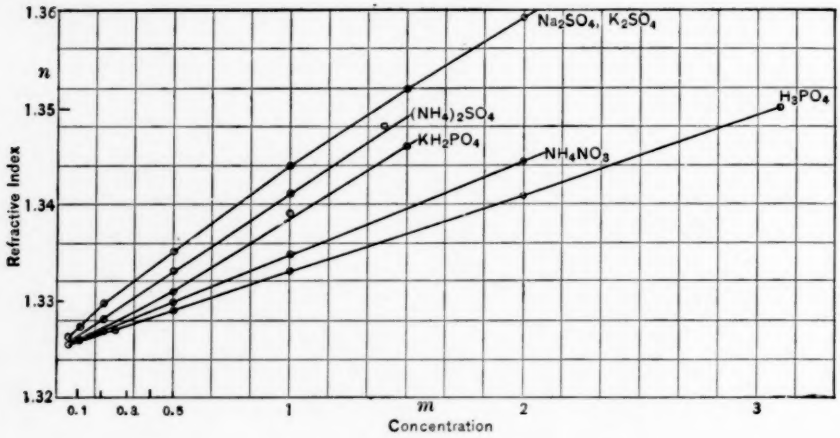

Fig. 13.

SUMMARY.

From the work that was done previous to this investigation, and from the data here presented, it is seen that with but few exceptions electrolytes in general give abnormal molecular depressions of the freezing-point in concentrated solutions. Among these exceptions are sodium, potassium and ammonium nitrates, and potassium dihydrogen phosphate.

Among the chlorides we observe that those of the second group in the periodic system give greater molecular depressions than those of the first group. We also observe that the curve for hydrochloric acid lies considerably above the corresponding curves for lithium, ammonium, sodium and potassium chlorides. The relation between lithium and the members of the second group is clearly shown by the curves for lithium chloride and lithium nitrate, which resemble the curves for the corresponding salts in the second group more closely than the analogues of the first group. The relation is very marked in the case of lithium nitrate.

Owing to limited solubility the study of the sulphates at great concentration was not possible, so that it cannot be stated whether or not these salts exhibit the phenomenon.

In general we may say that the freezing-point curve for any acid lies above those of the salts which it forms with the metals of the

first group, while it lies below the curves for its second group salts. Further, it will be seen that the molecular depressions for similar substances are arranged in the order of their molecular weights. The conductivity curves for all of the substances studied are perfectly normal throughout, showing absolutely no peculiarities in the region of dilution where the minimum of molecular depression manifests itself. The refractivity curves are nearly straight lines. In the few boiling-point curves which are given there is a more or less marked minimum, but as has already been pointed out, no great reliance can be placed upon the results obtained by the boiling-point method.

Conclusion.

The results obtained in this investigation can all be explained satisfactorily by the suggestion put forward by Jones and Chambers. We have attempted other explanations. The nature of many of the freezing-point curves suggests the curves obtained by Amagat[1] for gases. To these freezing-point curves we attempted to apply the well-known equation of Van der Waals:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

It, however, soon became obvious that without some radical modifications this equation could not be used.

Other suggestions met the same fate when tested by the experimentally established facts.

It should be added that the boiling-point determinations, as far as they have any value, point to the correctness of the suggestion that there are *hydrates formed in concentrated solutions.* The boiling-point curves show a minimum corresponding to the freezing-point curves. *The minimum in the boiling-point curves, however, is at greater concentration than in the freezing-point curves.* This is just what we should expect if the suggestion of the existence of hydrates in such solutions was correct. At the higher temperature the hydrates would be less stable, and would require greater concentration for their formation than at the lower temperature.

[1] Ann. Chim. Phys. [5], 19, 379, 1880.

Another strong line of evidence in favor of the existence of hydrates in concentrated solutions of electrolytes is the relation between the *water of crystallization* and the magnitude of the abnormal freezing-point lowerings. If hydrates exist in such solutions we should expect *those substances that crystallize with the greatest amount of water to be the ones that would form in solution the most complex hydrates.* That such is, in general, the fact, can be seen at once from Figs. 3, 4 and 5. Take Fig. 3, the chlorides of potassium, ammonium and sodium have no water of crystallization and give smaller lowering of the freezing-point of water than lithium chloride which crystallizes at low temperatures with two molecules of water; lithium chloride, in turn gives smaller lowering of the freezing-point than barium chloride which crystallizes at ordinary temperatures with two molecules of water. The chlorides of calcium and strontium, each with six molecules of water of crystallization, give still greater lowering of the freezing-point of water.

When we turn to Fig. 4, similar relations appear. Potassium, ammonium and sodium nitrates have no water of crystallization and all show comparatively small lowering of the freezing-point of water. Lithium nitrate with two and one half molecules of water of crystallization gives much greater lowering of the freezing-point of water than the remaining alkali nitrates; and it will be shown later by data now in hand, that the nitrates of the alkaline earths, with a greater number of molecules of water of crystallization, give still greater freezing-point lowering.

If we turn to Fig. 5, we see that sodium sulphate has water of crystallization, but the quantity depends on the conditions, and all of its water is held in very unstable equilibrium. The same remarks apply to sodium carbonate in Fig. 6.

A large number of similar relations will be pointed out in our next paper in the *American Chemical Journal*, April, 1904, and we have found many other relations of a similar character brought out by data now in hand, and which will be published in a few months.

All in all, the relations are so clean cut and unambiguous that we now do not hesitate to accept the conclusion *that hydrates exist in concentrated solutions of electrolytes.*

We have gone farther and *calculated the composition of such hydrates* for a number of substances, and the change in the composition of the hydrates of a given substance with change in the dilution of the solution.

These results were plotted as curves and will soon be published.[1] The curves expressing the relation between the composition of the hydrates and the concentration of the solutions, came out surprisingly smooth when we consider that every point on the curve contains no less than four experimentally determined values.

All things considered, then, the view which explains very satisfactorily our results is that originally suggested by Jones and Chambers, viz., that in the concentrated solutions there is combination between the molecules of the dissolved substance and the molecules of the solvent, thus removing a part of the solvent, as far as freezing-point lowering is concerned.

To explain the conductivity result it is also necessary to assume that there is a certain amount of electrolytic dissociation, together with the hydration, existing in these solutions.

We are extending this investigation to solvents other than water, to see whether a similar phenomenon manifests itself with non-aqueous solvents, and shall also study a much larger number of electrolytes in aqueous solution.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
November, 1903.

[1] Amer. Chem. Jour., April, 1904.

A METHOD FOR THE DETERMINATION OF COEFFICIENTS OF MUTUAL INDUCTION.

BY A. TROWBRIDGE.

THE principal methods for the determination of coefficients of mutual induction fall into three groups:

1. By comparison with self induction (which may be separately determined in absolute measure).[1]

2. By comparison with electrostatic capacity.[2]

3. By comparison with ohmic resistance.[3]

The first two are zero methods — the third is not, as it involves the use of a ballistic galvanometer.

For some time past I have been using a method in the laboratory which falls into group 1 and which has proved so satisfactory both as regards accuracy and simplicity that I publish it, thinking it may, for these reasons, commend itself. The very simplicity of the method made me at first suspect that it must have been adopted by others but on going over the literature of the subject as thoroughly as I am able, I find no description of the method.

Two coils of mutual inductance M and of self-inductances L_1 and L_2 when joined in series with the windings in the same direction are equivalant to a single coil of self-inductance equal to the sum of the coefficients of self-induction increased by twice the coefficient of mutual induction.

When the coils are joined in series so that the lines of force from one oppose the lines from the others, the system is equivalent to a single self-inductance equal to the sum of the coefficients of self-induction diminished by twice the coefficient of mutual induction.

The two coils (provided with a commutator for reversing the direction of the current through one of them) may be put in one branch of a Wheatstone bridge, the other branches of which consist of two noninductive resistances and a variable standard of self-induction.

[1] See Maxwell, "Electricity and Magnetism," Vol. II., 365, or Carhart and Patterson, "Electrical Measurements," p. 272.

[2] See Carey-Foster, Phil. Mag., 23, 121.

[3] See Glazebrook, Phil. Trans., 1883.

A balance for steady currents and for variable currents being obtained when the currents are in the same direction through the two coils gives $L' = L_1 + 2M + L_2$.

Repeating the balancing when the currents are in opposite directions through the two coils gives $L'' = L_1 - 2M + L_2$.

Combining these expressions gives $L' - L'' = 4M$ or $M = \frac{1}{4}(L' - L'')$. Thus M is got simply from the difference in the settings of the variable standard of self-induction in the two cases.

If such a standard is not available the determination of M becomes more tedious and may be effected as follows: A coil of self-inductance L may be prepared and used as a substitute for the variable standard mentioned above. It is well to choose the value of L about intermediate between L' and L''.

By the bridge method the ratios of L' to L and of L'' to L may be found — calling these p and q, respectively, the expression $M = 1/4 (L' - L'')$ becomes $M = L/4 (p - q)$.

If L be determined by balancing against electrostatic capacity then M may be calculated since p and q are numerical expressions obtained by the use of the bridge.

In the following table are given the results of a series of observations to determine the coefficients of mutual induction of a certian pair of coils. Those obtained with the aid of a variable standard are given in column I. Those obtained in the manner just described are given in the second column.

As a basis of comparison of the results obtainable by the method of reversing the coils with those obtainable by the same observer using some of the standard methods the coefficient of the coils was determined by the Maxwell method (group 1), by the Carey-Foster Method (group 2) and by the Glazebrook method (group 3).

The results are given in the third, fourth and fifth columns of the tables. The departures of the individual observations from the mean are also shown in each case.

The mutual induction consisted two similar circular brass frames 93.3 mm. in diameter, the annular region in which the wire was wound being 56.7 mm. in the plane of the windings and 22 mm. at right angles to it.

Each coil consisted of 23 turns per layer and 20 layers of No. 20 copper wire.

The resistance and self-inductance of each coil were respectively, 6.40 ohms and 0.0330 Henry.

All necessary precautions were taken to prevent the disturbing effects of thermal electromotive forces and of direct magnetic action of the coils on the galvanometer. The results given in the first four columns of the table were obtained by the use of a Thomson astatic galvanometer of 1070 ohms resistance and of sensibility of the order of 10^{-9} amperes.

The results shown in the last column were obtained by the use of a Nalder pattern ballistic galvanometer of 2400 ohms resistance of high sensibility adjusted to a period of about 5 seconds.

Table of determinations of M in Henrys by the various methods.

	I.	II.	III.	IV.	V.
	0.01535	0.01560	0.01567	0.01547	0.01528
	0.01545	0.01530	0.01564	0.01568	0.01504
	0.01540	0.01530	0.01542	0.01590	0.01499
	0.01535	0.01507	0.01510	0.01545	0.01528
	0.01548	0.01570	0.01564	0.01490	0.01470
Average,	0.01540	0.01539	0.01549	0.01548	0.01506

Table of departures of individual values from the mean.

	I.	II.	III.	IV.	V.
	−0.00005	+0.00021	+0.00018	−0.00001	+0.00022
	+0.00005	−0.00009	+0.00015	+0.00020	−0.00002
	±0.00000	−0.00009	−0.00007	+0.00042	−0.00007
	−0.00005	−0.00013	−0.00039	−0.00003	+0.00022
	+0.00008	+0.00031	+0.00015	−0.00050	−0.00036
Average,	0.00005	0.00021	0.00019	0.00023	0.00018

I am indebted to Miss Georgiana M. Whitcomb for her very conscientious work in obtaining the data contained in the table.

It appears that with the ordinary appliances of a laboratory equipped for advanced electrical measurements the first method is the most accurate, while the others show about an equal accuracy.

As regards the time required to perform the experiment, the first method has a very decided advantage.

Physical Laboratory of the University of Wisconsin,
November, 1903.

THE THEORY OF THE COMPOUND PENDULUM: CORRECTION.

By Robert R. Tatnall.

IN my paper on the Theory of the Compound Pendulum, in the Physical Review for December, 1903, I desire to correct an error, pointed out by my friend Lloyd Balderston, Jr., of the University of Pennsylvania.

After indicating the existence of a minimum period for a certain position of the sliding bob, between the centers of suspension and oscillation, I have, on p. 461, interpreted this fact to mean that a particle added below this minimum point would shorten the period, while a particle added higher up would lengthen the period. This is a mistake, since a particle added anywhere between the centers of suspension and oscillation will shorten the period, though the effect diminishes as the point of attachment approaches either of these centers, but nowhere changes sign within these limits. The same error appears again on p. 463, where it is implied that the example quoted from Routh is inconsistent with the fact of minimum period. There is, of course, no such inconsistency. The insertion of the two paragraphs concerned was entirely gratuitous, and the error thus introduced in no way affects the main argument of the paper, or the experimental evidence upon which it is established.

Mr. L. B. Tuckerman, Jr., of Ohio State University, has kindly pointed out that no imaginary values of x can occur in equation (5).

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

ON THE CHARACTER OF THE RADIATION FROM ORDINARY METALS.[1]

BY E. F. BURTON, B.A.

EXPERIMENTS made by a number of investigators[2] have shown that the conductivity of a mass of air confined in a closed metallic vessel depends upon the nature of the material of which the walls of the vessel are made. Patterson included in his experiments in this connection the determination of the conductivity of air at different pressures and found but little variation when using a small sheet-iron cylinder as the containing vessel when the pressure was reduced from one to about one third of an atmosphere; below a pressure of one third of an atmosphere he found the conductivity approximately proportional to the density of the air. From his results he deduced the conclusion that the conductivity of the confined air was probably due to the existence of an easily absorbed radiation from the walls of the receiver. In the conjoint paper by Professor McLennan and myself the results of a set of observations are given which fail to confirm the conclusions of Patterson. In our investigation it was found that the conductivity of ordinary air enclosed in a large galvanized-iron cylinder varied directly as the density over a range of pressures extending from 500 to 5 cm. of mercury. From this result we were led to conclude that the conductivity of the enclosed air was in a great measure due to a radiation not easily absorbed. Further experiments showed that part of this penetrating radiation, at least,

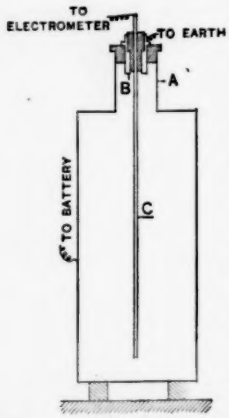

Fig. 1.

[1] Abstract of a paper presented at the meeting of the Physical Society held on December 30, 1903.

[2] McLennan and Burton, American Physical Society, Dec., 1902. Patterson, Proc. Camb. Phil. Soc., XII., p. 44. Strutt, Nature, Feb. 19, 1903.

had its source outside of the cylinder — a result confirmed by the experiments of Rutherford and Cook.[1]

The object of the experiments described in the present paper was to cut off entirely, if possible, this penetrating radiation from an external

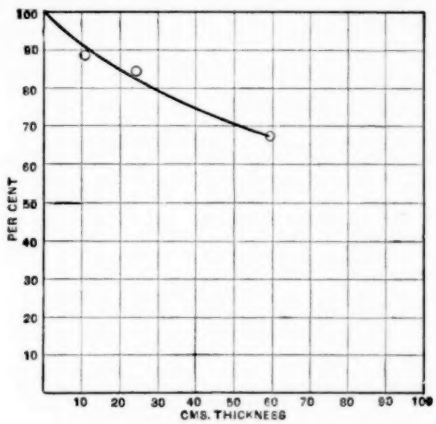

Fig. 2.

source and to determine the nature of the remaining radiation from the walls of the containing vessel.

The apparatus used was similar to that adopted in the experiment, referred to above. The air was enclosed in a cylinder of galvanized irons 125 cm. long and 30 cm. in diameter, such as that shown in Fig. 1. Into a tube *A*, about 20 cm. long, fastened into the top of the cylinder was fitted an ebonite plug about 5 cm. in diameter. A brass tube *B* was passed through this and into *B* a second ebonite plug was tightly fitted. The second plug carried a brass rod *C* which extended almost to the bottom of the cylinder. The brass tube *B*, which was earthed throughout the measurements, served as a guard tube and prevented any leak from the cylinder to the rod *C* across the ebonite plugs. The rod *C* was connected to a sensitive electrometer and the cylinder was kept charged to about 240 volts. The conductivity was measured by determining the saturation current through the enclosed air to the brass rod. In the attempts to cut off the external radiation the cylinder was immersed successively in water contained in tanks of different sizes, the whole being carefully insulated.

Tanks of three sizes were employed so as to give screens of water of thickness 10.5 cm., 24 cm., and 60 cm. respectively. The decrease in the conductivity in each case is shown in Table I.

[1] Rutherford and Cook, American Physical Society, Dec., 1902. Cook, Phil. Mag., Oct., 1903, p. 403.

TABLE I.

Thickness of Screen of Water.	Decrease in Conductivity.
10.5 cm.	11.9 per cent.
24	15.4 "
60	32.4 "

These values, which are approximately proportional to the thickness of the water layers surrounding the cylinder, are exhibited by the curve in Fig. 2, which shows that a water envelope of considerably greater thick-

TABLE II.

Pressure in mm.	Current — Arbitrary Scale.	Pressure in mm.	Current — Arbitrary Scale.
752	20.8	238	10.6
652	19.84	142	6.8
548	18.3	49	2.7
444	15.8	19	1.36
347	14.9		

ness than 60 cm. would be required in order to cut off completely the penetrating radiation. As apparatus suitable for this purpose was not available, the experiments with water screens were not carried further.

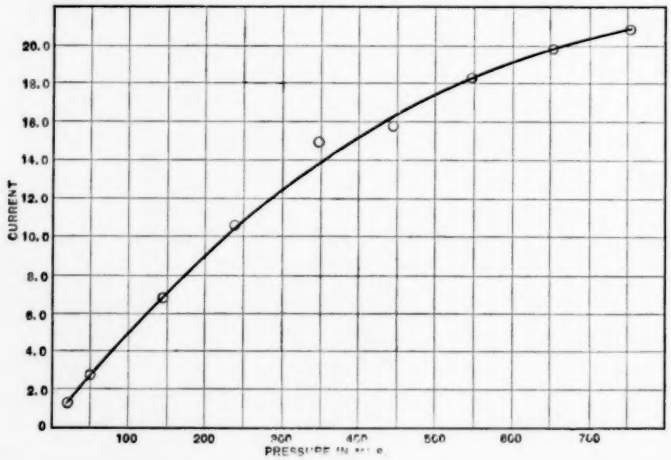

Fig. 3.

While the cylinder was immersed in the largest tank the pressure was reduced from 752 mm. of mercury to 19 mm. and the conductivity measured at various pressures. The values given in Table II. and represented

graphically in Fig. 3 show that again the conductivity is almost exactly proportional to the pressure and that, therefore, the remaining conductivity was due rather to a penetrating radiation than to one easily absorbed.

My most sincere thanks are due to Professor McLennan, under whose kind supervision the work was carried out.

NEW BOOKS.

Light for Students. By Edwin Edser. London, Macmillan, 1902. Pp. 574, 12.

This book has been written, according to the author's own statement in the preface, to meet the requirements of students who wish to obtain an accurate and comprehensive knowledge of geometrical and physical optics. The mathematical investigations have been rendered as simple as possible, the desire being to direct the attention to the physical aspect of the subject. The first 218 pages are devoted to the presentation of geometrical optics and the theory of optical instruments. The treatment of this branch of the science is clear, simple, complete, and in every way satisfactory.

The remaining 356 pages treat of the physical optics. In this portion of the book the author has included full explanations of many points not usually dealt with in works of similar scope, such as the investigation of the velocity of transverse waves in an elastic solid, and Sellmeier's theory of dispersion. He has however, found it impossible to include any mention of the electromagnetic theory. Although the electromagnetic theory is not discussed, electrons are introduced as the source of light waves on page 337; and, on page 348, we are told that "electric waves appear to be exactly similar to the waves producing ultraviolet, visible, and infra-red spectra." Also the mechanical pressure of light, which does not exist in the elastic solid theory of light, receives an interesting and satisfactory presentation on page 361.

Viewed, however, from the author's standpoint, namely that of imparting accurate knowledge, the value of the book is great, since it is a veritable storehouse of accurate and modern information. Hence it is indispensible as a book of reference, to the physicist and optician. We must however confess that we think its field of usefulness would have been much wider if more attention had been given to the imaginative side of the subject.

On page 457, the numerical value of the resolving power is given as only half as great as it should be, *i. e.*, it is found to be $Nn/2$ instead of Nn.

C. R. Mann.